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NEW APPROXIMATION FOR THE p(x) FUNCTION IN THE EVALUATION OF NON-ISOTHERMAL KINETIC DATA

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ABSTRACT

Three new approximations for the temperature integral, p(x), viz. a series, a three-term and a two-term, are proposed. The former two approximations have almost the same accuracy as the Scholmilch series, the percentage deviation being of the order of 10^{-6}. The linear dependence of x on ln p(x), of the slope d[ln $p(x)$]/dx on $1/x$ and of the intercept of the ln p(x) versus x curve on ln x have been established. A new equation for the evaluation of the kinetic parameters has been obtained from the above dependence which can be put in the form

$$\ln\frac{g(\alpha)}{T^{1.921503}} = \ln\frac{AE}{\phi R} + 3.772050 - 1.921503 \ln E - 0.120394(E/T)$$

The validity of this equation, based on the two-term approximation for p(x), has been tested with data from a theoretical thermogravimetric curve.

INTRODUCTION

Non-isothermal methods have been widely used to study the kinetics and mechanism of solid-state thermal decomposition reactions [1–5]. The basic equation generally employed for evaluating the kinetic parameters in non-isothermal methods is based on the formal kinetic equation used in homogeneous kinetics, viz.

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

in its modified form

$$\frac{d\alpha}{dT} = \frac{k(T)}{\phi}(1-\alpha)^n \tag{2}$$

where α, t, T, $k = k(T)$, n and ϕ are fraction decomposed, time, temperature, specific reaction rate, order parameter and linear heating rate, respectively. A more generalised form of eqn. (2) can be written as

$$\frac{d\alpha}{dT}=\frac{k(T)}{\phi}f(\alpha) \tag{3}$$

where $f(\alpha)$ has been defined as the conversion function, which depends on the mechanism of the process. For most reactions, $f(\alpha)$ has the form [6]

$$f(\alpha)=\alpha^m(1-\alpha)^n \tag{4}$$

where m and n are called the homogeneity factors. When $m=0$, eqn. (3) becomes the same as eqn. (2). The temperature-dependent rate constant, $k(T)$, is given by the Arrhenius equation

$$k(T)=A\,e^{-E/RT} \tag{5}$$

where A and E have the usual meaning. Substituting for $k(T)$, eqn. (3) can be re-written as

$$\frac{d\alpha}{dT}=\frac{A}{\phi}e^{-E/RT}f(\alpha) \tag{6}$$

Equations (3) and (6) can be integrated as follows.

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\int_{T_0}^T \frac{k(T)}{\phi}dT \tag{7}$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\frac{A}{\phi}\int_0^T e^{-E/RT}dT \tag{8}$$

In eqn. (8) the lower limit, T_0, is taken as zero for all practical purposes [7]. The left-hand side of eqn. (8) can be written as $g(\alpha)$, the correct form of which depends on the proper mechanism of the decomposition reaction [8]. If $f(\alpha)=(1-\alpha)^n$, then $g(\alpha)=[1-(1-\alpha)^{1-n}]/(1-n)$ when $n\neq 1$ and $-\ln(1-\alpha)$ when $n=1$. The integral on the right-hand side of eqn. (8) cannot be integrated in a closed form, because it is an incomplete gamma function. An incomplete gamma function has (i) a series solution [9–11] and (ii) a solution by numerical integration [6,12–14]. The series solution for an incomplete gamma function of the following form are given below.

$$\int_x^\infty \frac{e^{-u}}{u^b}du=Q(x)$$

Semi-convergent series

$$\int_x^\infty \frac{e^{-u}}{u^b}du=\frac{e^{-x}}{x^b}\left[1-\frac{b}{x}+\frac{b(b+1)}{x^2}\cdots +(-1)^j\frac{b(b+1)\dots(b+j-1)}{x^j}\right] \tag{9}$$

Scholmilch series

$$\int_x^{\infty} \frac{\mathrm{e}^{-u}}{u^b}\mathrm{d}u = \frac{\mathrm{e}^{-x}}{x^b}\left[1 - \frac{a_1}{(x+1)} + \frac{a_2}{(x+1)(x+2)} \cdots + \frac{(-1)^j a_j}{(x+1)(x+2)\ldots(x+j)}\right] \tag{10}$$

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

Rainville function, $(\mathrm{b})_0 = 1$

$$\int_x^{\infty} \frac{\mathrm{e}^{-u}}{u^b}\mathrm{d}u = x^{(1-b)}\,\mathrm{e}^{-x} \sum_{j=0}^{\infty} \frac{(-1)^j (b)_j}{x^{(j+1)}} \tag{11}$$

where $(b)_j = b(b+1)\,(b+2)\ldots(b+j-1)$.

In asymptotic expansions only a limited number of terms can be used for the calculation of the numerical values of $\mathrm{Q}(x)$. The temperature integral is only a special case of $\int_x^{\infty} (\mathrm{e}^{-u}/u^b)\,\mathrm{d}u$ with $x = E/RT$ and $b = 2$. A number of workers [6,7,12–19] have used different approximations for the evaluation of the temperature integral, $\mathrm{p}(x)$.

A NEW SERIES APPROXIMATION

In this communication we are introducing a new empirical approximation for the $\mathrm{p}(x)$ function which is given below.

$$\mathrm{p}(x) = \frac{\mathrm{e}^{-x}}{x^2}\left[1 - \frac{2}{(x+3)} - \frac{6}{(x+1)\ldots(x+3)} + \frac{28}{(x+1)\ldots(x+4)} - \frac{120}{(x+1)\ldots(x+5)} + \frac{496}{(x+1)\ldots(x+6)} - \frac{2016}{(x+1)\ldots(x+7)}\right] \tag{12}$$

Equation (12) can be generalised in the following form when $b \neq 1$

$$\int_x^{\infty} \frac{\mathrm{e}^{-u}}{u^b}\mathrm{d}u = \mathrm{Q}(x) = \frac{\mathrm{e}^{-x}}{x^b}\left[1 - \frac{b}{(x+b+1)} - \frac{b(b^2-1)}{(b-1)(x+1)\ldots(x+b+1)} + \frac{b^2(b^3-1)}{(b-1)(x+1)\ldots(x+b+2)} - \frac{b^3(b^4-1)}{(b-1)(x+1)\ldots(x+b+3)} + \frac{b^4(b^5-1)}{(b-1)(x+1)\ldots(x+b+4)} \cdots + \frac{(-1)^{(j-1)} b^{(j-1)}(b^j-1)}{(b-1)(x+1)\ldots(x+b+j)}\right] \tag{13}$$

when $b = 1$, eqn. (12) becomes

$$\int_x^\infty \frac{e^{-u}}{u^b} du = \frac{e^{-x}}{x^b}\left[1 - \frac{1}{(x+b+1)} - \frac{b(b-1)}{(x+1)(x+2)\dots(x+b+1)} + \frac{b^2(b^2+b+1)}{(x+1)\dots(x+b+2)} - \frac{b^3(b^3+b^2+b+1)}{(x+1)\dots(x+b+3)} + \frac{b^4(b^4+b^3+b^2+b+1)}{(x+1)\dots(x+b+4)}\dots + \frac{(-1)^{(j-1)}(b)^{(j-1)}(b)^{(j-1)}+b^{(j-2)}+b^{(j-3)}}{(x+1)\dots(x+j+1)} + \dots\right] \tag{13a}$$

Equation (12) can also be written in another simplified form as

$$p(x) = \frac{e^{-x}}{x^2}\left[1 - \frac{2}{(x+3)} - \frac{5}{(x+1)(x+2)(x+3)}\right] \tag{14}$$

A two-term approximation for eqn. (13) can be given as

$$Q(x) = \frac{e^{-x}}{x^b}\left[\frac{(x+1)}{(x+b+1)}\right] \tag{15}$$

when $b = 2$, eqn. (15) becomes

$$Q(x) = p(x) = \frac{e^{-x}}{x^2}\left[\frac{(x+1)}{(x+3)}\right] \tag{16}$$

which is the two-term approximation for the $p(x)$ function given by Van Tets [20].

The validity of eqns. (12), (14) and (16) has been tested with reference to semi-convergent series and Scholmilch series. The data are presented in Table 1. The $p(x)$ values calculated by the Van Tets approximation

$$p(x) = \frac{e^{-x}}{x^2}\left[1 - \frac{2}{(x+3)} - \frac{6}{(x+1)\dots(x+3)} + \frac{30}{(x+1)\dots(x+4)} - \frac{108}{(x+1)\dots(x+5)} + \frac{810}{(x+1)\dots(x+6)}\dots\right]$$

are also given for comparison.

EXPRESSION FOR p(x) FUNCTION

It has been established that $\ln p(x)$ varies linearly with x which can be put in the form

$$\ln p(x) = a + bx \tag{17}$$

TABLE 1

Comparison of p(x) values

x	$-\ln p(x)$					
	Semi-convergent series	Scholmilch approximation	Series approximation (eqn. 12)	Three-term approximation (eqn. 14)	Van Tets approximation	Two-term approximation (eqn. 16)
10	14.7785716	14.7753709	14.7752756	14.7756736	14.7750729	14.7722241
15	20.5352844	20.5349894	20.5350635	20.5350329	20.5349418	20.5338834
20	26.0830043	26.0829514	26.0829519	26.0829517	26.0829392	26.0824362
25	31.5121547	31.5121409	31.5121419	31.5121335	31.5121368	31.5118596
30	36.8650901	36.8650855	36.8650863	36.8650776	36.8650838	36.8649150

TABLE 2

Values of ln p(x), theoretical slope and intercept from $e^{-x}/x^2\,[(x+1)/(x+3)]$ approximation

x	$-\ln p(x)$	Slope (b)	Intercept (a)
20	26.0824362	−1.0958592	−4.1652523
25	31.5118596	−1.0772527	−4.5805415
30	36.8649151	−1.0647116	−4.9235670
35	42.1647633	−1.0556809	−5.2159315
40	47.4253870	−1.0488656	−5.4707630
45	52.6558846	−1.0435386	−5.6966471
50	57.8625123	−1.0392601	−5.8995000
55	63.0497577	−1.0357479	−6.0836226
60	68.2209500	−1.0328129	−6.2517610
65	73.3786275	−1.0303236	−6.4059315
70	78.5247700	−1.0281856	−6.5517780
75	83.6609517	−1.0263293	−6.6862535
80	88.7884447	−1.0247025	−6.8122441
85	93.9082920	−1.0232651	−6.9307585
90	99.0213593	−1.0219859	−7.0426280
95	104.1283731	−1.0208400	−7.1485730
100	109.2299488	−1.0198078	−7.2491788

A closer examination of eqn. (17) shows that the intercept, a, and slope, b, vary linearly with ln x and $1/x$, respectively. These relations can be represented as

$$a = a_1 + a_2 \ln x \tag{18}$$

$$b = b_1 + \frac{b_2}{x} \tag{19}$$

When the values of a and b are substituted in eqn. (17), we have

$$\begin{aligned} \ln p(x) &= a_1 + a_2 \ln x + \left(b_1 + \frac{b_2}{x}\right)x \\ &= a_1 + b_2 + a_2 \ln x + b_1 x \end{aligned} \tag{20}$$

or

$$p(x) = e^{(a_1+b_2)} x^{a_2}\, e^{b_1 x} \tag{21}$$

Ln p(x) values were calculated using eqn. (16) for $x = 20(5)$–100. These values are given in Table 2. The theoretical slope d[ln p(x)]/dx was calculated from eqn. (16) as

$$\frac{d[\ln p(x)]}{dx} = \text{slope} = b = -1 - \frac{2}{x} + \frac{1}{(x+1)} - \frac{1}{(x+3)}$$

The theoretical intercept, $a = \ln p(x) - bx$, was also calculated; the corresponding numerical values of slopes and intercepts are given in Table 2.

From the linear plot of slope versus $1/x$, b_1, b_2 and the correlation coefficient, r, were calculated and their values are as follows: $b_1 = -1.000953$, $b_2 = -1.907067$, $r = 0.999973$. The values of a_1, a_2 and correlation coefficient, r, for the linear plot of intercept versus $\ln x$ are: $a_1 = 1.609487$, $a_2 = -1.921503$, $r = 0.999966$. On substituting the numerical values of a_1, a_2 and b_1, b_2, eqn. (20) becomes

$$-\ln \mathrm{p}(x) = 0.297580 + 1.921503 \ln x + 1.000953x \qquad (22)$$

When $x = E/RT$ and $R = 8.314$ J mol^{-1} K^{-1} are introduced in eqn. (22), then

$$-\ln \mathrm{p}(E/RT) = -3.772050 + 1.921503 \ln(E/T) + 0.120394(E/T) \qquad (23)$$

In eqn. (22) we have shown that $\ln \mathrm{p}(x)$ is a linear function of x, and the slopes and the intercepts are linear functions of $1/x$ and $\ln x$, respectively. This means that $\ln \mathrm{p}(x)$ will vary linearly with $1/T$ as well as with E at constant E and at constant T, respectively. It is also found that the intercepts obtained from $\ln \mathrm{p}(x)$ versus $1/T$ and $\ln \mathrm{p}(x)$ versus E can be related to $\ln E$ and $\ln T$, respectively. When $x = E/RT$ is substituted for $\mathrm{p}(x)$ in eqn. (16), we get

$$\mathrm{p}(x) = \frac{R^2T^2}{E^2} \mathrm{e}^{-E/RT} \left[\frac{E + RT}{E + 3RT}\right] \qquad (24)$$

Therefore

$$-\ln \mathrm{p}(x) = -2 \ln R - 2 \ln T + 2 \ln E + E/RT - \ln(E + RT) + \ln(E + 3RT)\ldots \qquad (25)$$

In eqn. (24) E and T are variables.

The numerical values of $\ln \mathrm{p}(x)$ were evaluated using Scholmilch approximation [21] for various values of E ($E = 60(10)$–400 kJ mol^{-1}) at constant T and for various values of T ($T = 300(10)$–800 K) at constant E. The variations of $\ln \mathrm{p}(x)$ with $1/T$ at constant E can be put in the form

$$\ln \mathrm{p}(x) = A + B/T \qquad (26)$$

The slope, B, and the intercept, A, were calculated and these are given in Table 3. It is found that the slope, B, varies linearly with E and, therefore, the relation becomes

$$B = B_1 + B_2 E \qquad (27)$$

The intercept, A, is also related to $\ln E$

$$A = A_1 + A_2 \ln E \qquad (28)$$

Combining eqns. (27) and (28) with eqn. (26)

$$\ln \mathrm{p}(x) = A_1 + A_2 \ln E + \left(\frac{B_1 + B_2 E}{T}\right) \qquad (29)$$

TABLE 3

Values of slope, intercept and correlation coefficient for log p(x) versus $1/T$ plots at constant E

E (kJ mol^{-1})	Slope (B)	Intercept (A)	r
60.0	-0.3530613×10^4	-1.546872	0.99990196
70.0	-0.4055747×10^4	-1.667876	0.99992385
80.0	-0.4580284×10^4	-1.773858	0.99993912
90.0	-0.5104400×10^4	-1.868167	0.99995022
100.0	-0.5628208×10^4	-1.953137	0.99995852
110.0	-0.6151784×10^4	-2.030464	0.99996490
120.0	-0.6675810×10^4	-2.101418	0.99996991
130.0	-0.7198434×10^4	-2.166975	0.99997392
140.0	-0.7721574×10^4	-2.227903	0.99997717
150.0	-0.8244619×10^4	-2.284814	0.99997985
160.0	-0.8767587×10^4	-2.338208	0.99998209
170.0	-0.9290490×10^4	-2.388496	0.99998397
180.0	-0.9813338×10^4	-2.436021	0.99998557
190.0	-0.1033614×10^5	-2.481071	0.99998694
200.0	-0.1085890×10^5	-2.523892	0.99998812
210.0	-0.1138163×10^5	-2.564695	0.99998915
220.0	-0.1190432×10^5	-2.603662	0.99999006
230.0	-0.1242699×10^5	-2.640952	0.99999085
240.0	-0.1294963×10^5	-2.676703	0.99999155
250.0	-0.1347226×10^5	-2.711037	0.99999217
260.0	-0.1399486×10^5	-2.744064	0.99999273
270.0	-0.1451745×10^5	-2.775878	0.99999323
280.0	-0.1504002×10^5	-2.806565	0.99999368
290.0	-0.1556258×10^5	-2.836204	0.99999409
300.0	-0.1608513×10^5	-2.864864	0.99999446
310.0	-0.1660767×10^5	-2.892606	0.99999479
320.0	-0.1713019×10^5	-2.919489	0.99999509
330.0	-0.1765271×10^5	-2.945563	0.99999538
340.0	-0.1817522×10^5	-2.970877	0.99999563
350.0	-0.1869772×10^5	-2.995473	0.99999587
360.0	-0.1922021×10^5	-3.019391	0.99999609
370.0	-0.1974270×10^5	-3.042667	0.99999629
380.0	-0.2026518×10^5	-3.065335	0.99999647
390.0	-0.2078765×10^5	-3.087426	0.99999664
400.0	-0.2131012×10^5	-3.108969	0.99999680

The numerical values of the constants A_1, A_2, B_1, B_2 and the correlation, coefficient, r, for the linear plots are given below (base 10 logarithms were used in these calculations). For a slope versus E plot: $B_1 = -0.400808 \times 10^3$, $B_2 = -5.227990 \times 10^{-2}$, $r = 0.99999992$. For an intercept versus log E plot: $A_1 = 7.575626$, $A_2 = -1.906026$, $r = 0.99993945$. The log(intercept) versus log E plot has a correlation coefficient of 0.999220, but the intercept versus ln E plot gives a much higher correlation coefficient (0.99993945); hence, we chose the latter. Keeping T constant, the variations of $\ln p(x)$ versus E were evaluated and the relation can be represented as

$$\ln p(x) = X + YE \tag{30}$$

The values of the slope, Y, intercept, X, and the correlation coefficient for the plots are given in Table 4. X and Y were also related to $1/T$ and $\ln T$, respectively. The relations can be put in the form

$$Y = Y_1 + Y_2/T \tag{31}$$

$$X = X_1 + X_2 \ln T \tag{32}$$

Combining eqns. (31) and (32) with eqn. (30), $\ln p(x)$ becomes

$$\ln p(x) = X_1 + X_2 \ln T + (Y_1 + Y_2/T)E \tag{33}$$

The numerical values of X_1, X_2, Y_1, Y_2 and r are given below (data are to $\log_{10}$). Slope versus $1/T$ plot: $Y_1 = -0.418466 \times 10^{-5}$, $Y_2 = -5.227990 \times 10^{-2}$, $r = 0.99999998$. Intercept versus $\log T$ plot: $X_1 = -7.568931$, $X_2 = 1.908397$, $r = 0.99998649$. Since the intercept versus $\log T$ plot has a better correlation than the log(intercept) versus $\log T$ plot, the former is chosen. Therefore, the two equations can be written as:

$$\begin{aligned} -\log p(x) = {} & -7.575626 + 1.906026 \log E \\ & + (0.400808 \times 10^3 + 5.227990 \times 10^{-2} E)/T \end{aligned} \tag{34}$$

$$\begin{aligned} -\log p(x) = {} & 7.568931 - 1.908397 \log T \\ & + (0.418466 \times 10^{-5} + 5.227990 \times 10^{-2}/T)E \end{aligned} \tag{35}$$

Zsako [6] has given the relation between $\ln g(\alpha)$ and $\ln p(x)$ as

$$\ln g(\alpha) - \ln p(x) = \ln \frac{AE}{\phi R}$$

On substituting the values of $p(x)$ from eqn. (23) and transposing

$$\ln g(\alpha) = \ln \frac{AE}{\phi R} + 3.772050 - 1.921503 \ln(E/T) - 0.120394(E/T) \tag{36}$$

or

$$\ln\left[\frac{g(\alpha)}{T^{1.921503}}\right] = \ln \frac{AE}{\phi R} + 3.772050 - 1.921503 \ln E - 0.120394(E/T) \tag{37}$$

The plot of the left-hand side of eqn. (37) against $1/T$ gives a linear curve; the slope is equal to $-0.120394E$ and the intercept equals $\ln(AE/\phi R) + 3.772050 - 1.921503 \ln E$, which on simplification gives

$$\text{intercept} = \ln(A/\phi) - 0.921503 \ln E - 5.889991$$

E and A can be calculated from the slope and the intercept, respectively.

TABLE 4

Values of slope, intercept and correlation coefficient for log p(x) versus E plots at constant T

T(K)	Slope (Y)	Intercept (X)	r
300	-1.784371×10^{-4}	−2.844525	0.99998301
310	-1.728183×10^{-4}	−2.816869	0.99998192
320	-1.675506×10^{-4}	−2.790115	0.99998080
330	-1.626020×10^{-4}	−2.764207	0.99997965
340	-1.599445×10^{-4}	−2.739094	0.99997847
350	-1.535532×10^{-4}	−2.714731	0.99997726
360	-1.494053×10^{-4}	−2.691074	0.99997602
370	-1.454819×10^{-4}	−2.668086	0.99997476
380	-1.417647×10^{-4}	−2.645729	0.99997346
390	-1.382081×10^{-4}	−2.623972	0.99997214
400	-1.348877×10^{-4}	−2.602784	0.99997079
410	-1.317001×10^{-4}	−2.582136	0.99996941
420	-1.286654×10^{-4}	−2.562003	0.99996808
430	-1.257712×10^{-4}	−2.542369	0.99996658
440	-1.230084×10^{-4}	−2.523184	0.99996513
450	-1.203684×10^{-4}	−2.504455	0.99996362
460	-1.177843×10^{-4}	−2.486152	0.99996212
470	-1.154251×10^{-4}	−2.468258	0.99996058
480	-1.131079×10^{-4}	−2.450755	0.99995904
490	-1.108852×10^{-4}	−2.433627	0.99995742
500	-1.087513×10^{-4}	−2.416858	0.99995584
510	-1.067010×10^{-4}	−2.400435	0.99995418
520	-1.047295×10^{-4}	−2.384343	0.99995252
530	-1.028324×10^{-4}	−2.368570	0.99995084
540	-1.010054×10^{-4}	−2.353105	0.99994913
550	-9.924488×10^{-5}	−2.337935	0.99994739
560	-9.754714×10^{-5}	−2.323051	0.99994563
570	-9.590891×10^{-5}	−2.308441	0.99994385
580	-9.432713×10^{-5}	−2.294097	0.99994204
590	-9.279890×10^{-5}	−2.280008	0.99994021
600	-9.132157×10^{-5}	−2.266167	0.99993837
610	-8.989262×10^{-5}	−2.252566	0.99993649
620	-8.850972×10^{-5}	−2.239196	0.99993460
630	-8.717067×10^{-5}	−2.226051	0.99993268
640	-8.587334×10^{-5}	−2.213120	0.99993074
650	-8.461604×10^{-5}	−2.200401	0.99992878
660	-8.339672×10^{-5}	−2.187886	0.99992679
670	-8.221374×10^{-5}	−2.175568	0.99992479
680	-8.106552×10^{-5}	−2.163441	0.99992276
690	-7.995054×10^{-5}	−2.151501	0.99992072
700	-7.886737×10^{-5}	−2.139741	0.99991865
710	-7.781467×10^{-5}	−2.128156	0.99991656
720	-7.679117×10^{-5}	−2.116742	0.99991445
730	-7.579567×10^{-5}	−2.105497	0.99991232
740	-7.482704×10^{-5}	−2.694407	0.99991018
750	-7.388420×10^{-5}	−2.083476	0.99990801
760	-7.296613×10^{-5}	−2.072698	0.99990582
770	-7.207188×10^{-5}	−2.062069	0.99990361
780	-7.120051×10^{-5}	−2.051585	0.99990139
790	-7.035117×10^{-5}	−2.041241	0.99989914
800	-6.952303×10^{-5}	−2.031035	0.99989690

VALIDITY OF THE PROPOSED APPROXIMATION.

The validity of the simple approximation, viz. $p(x) = e^{-x}/x^2\ [(x+1)/(x+3)]$, was tested by introducing the kinetic data from a theoretical TG curve in eqn. (37). Theoretical T values were generated using the first-order equation along with the two-term approximation for the $p(x)$ function. Arbitrary values of $E = 100$ kJ mol^{-1}, $A = 1 \times 10^{10}$ s^{-1}, $\phi = 10$°C min^{-1} and $R = 8.314$ J mol^{-1} K^{-1} were used in eqn. (38), which is given below.

$$-\ln(1-\alpha) = g(\alpha) = \frac{ART^2}{\phi E} e^{-E/RT}\left[\frac{(E+RT)}{(E+3RT)}\right] \tag{38}$$

T values were calculated by an iteration method for α ranging from 0.05 to 0.95 with an increment of 0.05 and T ranging from 300 to 800 K with a 0.001 increment. The theoretical values of T are given in Table 5. Using these T values, E was recalculated using eqn. (37). Similar plots were drawn for the Coats–Redfern [22] and MacCallum–Tanner [23] equations for comparison. The E values obtained from the three equations and the percentage deviations from the theoretical value are given in Table 6. The

TABLE 5

Theoretical T values for different α

α	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95
T(K)	396.736	405.916	411.608	415.859	419.324	422.297	424.297	427.353	429.603	431.739	433.802	435.825	437.844	439.895	442.025	444.301	446.835	449.856	454.023

TABLE 6

Comparison of E values for different approximations

Approximation/equation	E (kJ mol^{-1})	% deviation from theoretical value [a]
(1) Equation (37) of present work		
$\ln\left[\frac{g(\alpha)}{T^{1.921503}}\right] = \ln\frac{AE}{\phi R} + 3.77205 - 1.921503 \ln E - 0.120394(E/T)$	99.6266	0.3734
(2) Coats and Redfern		
$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$	99.4384	0.5616
(3) MacCallum and Tanner		
$\log g(\alpha) = \log\frac{AE}{\phi R} - 0.483E^{0.435} - \frac{(0.449 + 0.217E) \times 10^3}{T}$	98.6046	1.3954

[a] Theoretical value of $E = 100$ kJ mol^{-1}.

observed deviations from the theoretical E value are 0.3734, 0.5616 and 1.3954% for eqn. (37) (present work), Coats–Redfern and MacCallum–Tanner equations, respectively.

The validity of our approximation was further confirmed by the E value computed from Gyulai and Greenhow theoretical TG data [24]. When these data were introduced in eqn. (37), the E value obtained by us is 251.093 kJ mol^{-1} whereas that calculated by Gyulai and Greenhow is 251.333 kJ mol^{-1}; the theoretical value of E assumed by these authors is 251.160 kJ mol^{-1}.. The percentage error for the two approximations is 0.0267 and 0.0689, respectively, from the theoretical value ($E = 251.160$ kJ mol^{-1}).

CONCLUSION

The series approximation given by eqn. (12) and the approximation given by Scholmilch [21]

$$\mathrm{p}(x) = \frac{\mathrm{e}^{-x}}{x^2}\left[1 - \frac{2}{(x+1)} + \frac{4}{(x+1)(x+2)} - \frac{10}{(x+1)\ldots(x+3)} + \frac{30}{(x+1)\ldots(x+4)} - \frac{148}{(x+1)\ldots(x+5)}\ldots\right]$$

give close values of p(x), and the percentage deviation between the two is 1.92×10^{-6} (for $x = 20$).

The three-term approximation for p(x) given in eqn. (14) also agrees very well with the Scholmilch approximation. It is found that the approximation used in eqn. (14) is much superior to all other approximations with a minimum percentage deviation of 1.15×10^{-6} (for $x = 20$).

Equation (23) gives close values of E for the theoretically generated TG curve which indicates that the intercept from ln p(x) versus $1/T$ or E plots can be linearly related to ln E or ln T better than ln(intercept) versus ln E or ln T.

Equation (37) which employs $T^{1.921503}$ in place of T^2 as in the Coats and Redfern equation, gives values of E closer to the theoretical value. Similarly, eqn. (37) gives more accurate E values than those from the Coats–Redfern and MacCallum–Tanner equations. Therefore, eqn. (37), based on the two-term approximation proposed in the present work, is the best suited solution for the evaluation of kinetic parameters from thermogravimetric (TG) experiments.

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