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New equations for kinetic analysis of non-isothermal reactions

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Abstract

Kinetic equations of the form $\ln[g(\alpha)/T^{c''}] = \ln[AE/\phi R] + c' - c'' \ln E - c'''(E/T)$ are proposed for the evaluation of activation parameters from non-isothermal experiments. The values of c', c'' and c''' have been derived using the already established linear dependence of (i) the logarithm of the Arrhenius temperature integral $\ln p(x)$ on x $(= E/RT)$, (ii) its slope on x^{-1}, and (iii) its intercept on $\ln x$, respectively. The $\ln p(x)$ values were computed from the recently proposed series and the closed-form three-term approximations. The kinetic parameters computed with the proposed equations show better agreement for theoretical TG curves than do the well known methods. The equations have equal practical significance in the kinetic analysis of non-isothermal processes.

INTRODUCTION

Non-isothermal methods have been extensively used for the study of the kinetics and mechanism of condensed phase reactions [1]. The temperature dependence of many of these reactions has been shown to be Arrhenius-type. The Arrhenius equation, $k = A\,\mathrm{e}^{-E/RT}$ (where A is the pre-exponential factor and E the activation energy of a reaction), is generally used as such for the evaluation of activation parameters from isothermal measurements. However, in non-isothermal experiments with a linear heating rate ϕ, the integral form of the rate expression becomes $\int_0^\alpha \mathrm{d}\alpha/f(\alpha) = A/\phi \int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T$. (The left-hand side of the equation is the conversion integral, $g(\alpha)$.) The right-hand side of the rate equation involving the exponential integral has no closed-form solutions. If $E/RT = x$, the integral $\int_0^T \mathrm{e}^{-E/RT}\,\mathrm{d}T$ is transformed into $\int_x^\infty (\mathrm{e}^{-x}/x^2)\,\mathrm{d}x$, which is a special case of the incomplete gamma function $\int_x^\infty (\mathrm{e}^{-u}/u^b)\,\mathrm{d}u$ (where

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$u = x$ and $b = 2$), which has either a series solution [2,3] or a solution by numerical integration [4–6]. This integral is known as the Arrhenius temperature integral which has been generally called the $p(x)$ function [7]. The most important generalized series solutions for $p(x)$ are asymptotic expansions and Scholmilch series. Computed values of the temperature integral $p(x)$, with different values of activation energy E and temperature T, are generally employed in non-isothermal kinetic analysis.

In the present paper we introduce a new series approximation and a closed-form three-term approximation for the computation of the Arrhenius temperature integral, $p(x)$. The dependence of the values of $p(x)$ on the energy of activation and reaction temperature has been made use of to derive two corresponding kinetic equations for the evaluation of non-isothermal data. The validity of the new equations has been confirmed by the analysis of theoretical and experimental thermogravimetric curves.

A NEW APPROXIMATION

We have proposed [8] a new series approximation for the incomplete gamma function $Q(x)$

$$\begin{aligned}\int_x^\infty \frac{e^{-u}}{u^b}\,du &= Q(x)\\ &= \frac{e^{-x}}{x^b}\left[1 - \frac{b}{(x+b+1)} - \frac{b(b^2-1)}{(b-1)(x+1)\ldots(x+b+1)}\right.\\ &\quad + \frac{b^2(b^3-1)}{(b-1)(x+1)\ldots(x+b+2)} - \frac{b^3(b^4-1)}{(b-1)(x+1)\ldots(x+b+3)}\\ &\quad + \frac{b^4(b^5-1)}{(b-1)(x+1)\ldots(x+b+4)}\ldots\\ &\quad \left. + \frac{(-1)^{(j-1)}b^{(j-1)}(b^j-1)}{(b-1)(x+1)\ldots(x+b+j)}\right] \qquad (1)\end{aligned}$$

where $b \neq 1$.

The generalized series solution given in eqn. (1) is closely related to the Scholmilch approximation [2]. For ease of computation, we also proposed a shorter closed-form three-term approximation

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

in which the third term represents the approximate sum of all the terms beyond the second term of eqn. (1). Substituting $b = 2$, eqns. (1) and (2) become eqns. (3) and (4) respectively, which give the Arrhenius tempera-

TABLE 1

Various approximations for the temperature integral $p(x)$

Scholmilch [2]

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

Semi-convergent series [8]

$$p(x)=\frac{\mathrm{e}^{-x}}{x^2}\left[1-\frac{2}{x}+\frac{6}{x^2}-\frac{24}{x^3}+\frac{120}{x^4}-\frac{720}{x^5}+\ldots\right]$$

Two-term [8]

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

Van Tets [9]

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

Senung and Yang [10]

$$p(x)=\frac{\mathrm{e}^{-x}}{x}\left[\frac{(x^2+10x+18)}{(x^3+12x^2+36x+24)}\right]$$

Reich and Stivala [11]

$$p(x)=\frac{\mathrm{e}^{-x}}{x}\left[\frac{(x+4)}{(x^2+6x+6)}\right]$$

Gorbachev [12]

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

Zsako [13]

$$p(x)=\mathrm{e}^{-x}\left[\frac{1}{(x+2)(x-d)}\right]\quad\text{where}\quad d=16/(x^2+4x+84)$$

Flynn and Wall [14]

$$p(x)=\frac{\mathrm{e}^{-x}}{x}\left[0.0000035+\frac{0.99871}{x}-\frac{1.9848764}{x^2}\right.$$
$$\left.+\frac{4.9482092}{x^3}-\frac{11.7850792}{x^4}+\ldots\right]$$

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ture integral $p(x)$

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

$$p(x) = \frac{e^{-x}}{x^2}\left[1 - \frac{2}{(x+3)} - \frac{5}{(x+1)(x+2)(x+3)}\right] \tag{4}$$

The validity of the proposed approximations for $p(x)$ given in eqns. (3) and (4) was tested with reference to the Scholmilch series, the series that gives closest agreement to the numerically integrated values. A comparison is also made with the other approximations proposed by earlier workers [8–14]. These approximations and the comparative data for $p(x)$ for a typical value of $x = 20$, are given in Tables 1 and 2 respectively. The $\ln p(x)$ values from our approximation, i.e. the series and three-term, are nearest to those of the reference Scholmilch approximation, the deviation being of the order of 1.7×10^{-6}%.

LINEARIZATION OF THE $p(x)$ FUNCTION

The expression for the $p(x)$ function shows that it is a function of E and $1/T$ [4–6, 15], i.e.

$$p(x) = f(E, 1/T) \tag{5}$$

Because E and $1/T$ separately approximate to linear functions of $\ln p(x)$, we have tried to establish their combined dependence on $\ln p(x)$. For the

TABLE 2

Comparison of $\ln p(x)$ from different approximations for $x = 20$

Approximations	$-\ln p(x)$	% deviation from Scholmilch × 10^6
Scholmilch	26.0829514	–
Semi-convergent	26.0830043	202.8
Series	26.0829519	1.9
Three-term	26.0829518	1.5
Two-term	26.0824362	1975.2
Van Tets	26.0829392	46.8
Senung and Yang	26.0829427	33.3
Reich and Stivala	26.0829797	108.5
Gorbachev	26.0867747	1465.8
Zsako	26.0847926	7059.0
Flynn and Wall	26.0852989	9000.1

TABLE 3

Values of correlation constants for β versus $1/x$ and I versus $\ln x$ plots

Approximations	β versus $1/x$ (eqn. (7))			I versus $\ln x$ (eqn. (6))		
	b_1	b_2	r	a_1	a_2	r
Series	−1.001928	−1.817191	0.999909	1.427514	−1.884318	0.999918
Three-term	−1.000974	−1.905622	0.999959	1.605659	−1.920620	0.999960

linear relation of $\ln p(x)$ and x, i.e. $\ln p(x) = I + \beta x$, the numerical values of the theoretical slope, $\beta = (\mathrm{d}\ln p(x)/\mathrm{d}x)$, and the intercept, $I = (\ln p(x) - (\beta x))$, for $x = 20(5)100$ have been evaluated using the series solution (eqn. (3)) and three-term approximation (eqn. (4)). As observed earlier [8], it is seen that the slope β is linearly related to x^{-1} and the intercept I to $\ln x$, which can be expressed in the following forms:

$$I = a_1 + a_2 \ln x \tag{6}$$

$$\beta = b_1 + b_2/x \tag{7}$$

The numerical values of the curve fit constants for the above equations for the series and three-term approximation are given in Table 3. The correlation coefficients (r) are above 0.9999 for both plots, indicating the validity of our assumptions regarding the linear relations. Substituting eqns. (6) and (7) in the linear relation of $\ln p(x)$ and x

$$\ln p(x) = a_1 + a_2 \ln x + (b_1 + b_2/x)x \tag{8}$$

which shows the combined dependence of E and $1/T$ on $p(x)$. Inserting the numerical values of a_1, a_2, b_1 and b_2 in eqn. (8) and rearranging, we get the following equations for $p(x)$:

For the series solution

$$-\ln p(x) = 0.38968 + 1.8843 \ln x + 1.00193x \tag{9}$$

For the three-term approximation

$$-\ln p(x) = 0.29996 + 1.9206 \ln x + 1.00097x \tag{10}$$

DISCUSSION

The Arrhenius temperature integral, $p(x)$ or $p(E/RT)$, has been widely employed in non-isothermal kinetic analysis by suitable rearrangement for linearization. The relation between the conversion integral $g(\alpha) =$

$\int_0^\alpha \mathrm{d}\alpha/f(\alpha)$ and the temperature integral $p(x)$ can be represented as

$$g(\alpha) = AE/\phi R\left[\mathrm{e}^{-x}/x + \int_x^\infty (-\mathrm{e}^x/x)\,\mathrm{d}x\right]$$

$$= (AE/\phi R)p(x) \tag{11}$$

Zsako [4] attempted to simplify this relation by using a logarithm form of eqn. (11)

$$\ln g(\alpha) - \ln p(x) = \ln(AE/\phi R) \tag{12}$$

where ϕ is the heating rate and R the gas constant. Thus, the activation parameters E and A can be calculated from eqn. (12) if $g(\alpha)$ and $p(x)$ are known.

Introducing eqns. (9) and (10) for $\ln p(x)$ in the above relation and on transposing, we obtain

$$\ln g(\alpha) = \ln(AE/\phi R) - 0.38968 - 1.8843 \ln x + 1.00193x \tag{13}$$

$$\ln g(\alpha) = \ln(AE/\phi R) - 0.29996 - 1.9206 \ln x + 1.00097x \tag{14}$$

Substituting $x = E/RT$ and $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$ in eqns. (13) and (14), yields the final forms of the kinetic equations, eqns. (15) and (16), for the series solution and the closed-form three-term approximations respectively

$$\ln[g(\alpha)/T^{1.8843}] = \ln(AE/\phi R) + 3.6012 - 1.8843 \ln E - 0.12051(E/T) \tag{15}$$

$$\ln[g(\alpha)/T^{1.9206}] = \ln(AE/\phi R) + 3.7678 - 1.9206 \ln E - 0.12040(E/T) \tag{16}$$

The plot of left-hand side of eqns. (15) or (16) versus reciprocal absolute temperature will give linear curves, and E and A can be calculated from the slope and intercept respectively. Equations (15) and (16) are similar to the equation that we proposed in ref. 8, except for the numerical values of the constants c', c'' and c'''.

VALIDITY OF THE PROPOSED APPROXIMATIONS/EQUATIONS

The validity of the two approximations and of eqns. (15) and (16) derived from them, was tested by theoretical and experimental thermogravimetric data, because TG is one of the most widely used techniques for evaluating activation parameters for solid state thermal decomposition reactions. A theoretical TG curve was generated for the value of $E = 100\ \mathrm{kJ\ mol^{-1}}$, $A = 1 \times 10^{10}\ \mathrm{s^{-1}}$ and heating rate = $10°\mathrm{C\ min^{-1}}$. These values of E, A and ϕ were introduced in a first-order kinetic equation making use of the series and three-term approximations. Using a computer, temperature values were generated by an iteration method described by us earlier [8] for α values in the range 0.05–0.95 and temperature in the range 370–1000 K. The generated temperature values are identical up to five significant figures in all cases for the two approximations. Using these temperature values and

TABLE 4

Comparison of activation energy and correlation coefficients from theoretical TG data

Equations	$E/(\text{kJ mol}^{-1})$	r	Percentage deviation from theoretical E[a]
Equation (15)	99.97[b]	0.99999992	0.03
Equation (16)	99.93[c]	0.99999994	0.07
Coats–Redfern	99.65[b]	0.99999990	0.35
	99.65[c]	0.99999987	0.35
McCallum–Tanner	99.00[b]	0.99999899	1.00
	99.00[c]	0.99999896	1.00

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

[b] E values computed using temperatures generated from the series approximation.

[c] E values computed using temperatures generated from the three-term approximation.

the corresponding α values, Arrhenius plots were made and activation energy was calculated using eqns. (15) and (16). The correlation coefficients r for the two plots are 0.99999992 and 0.99999994 respectively, indicating perfect linear fits. These values of E and r are given in Table 4. The kinetic constants calculated using the newly derived equations, eqns. (15) and (16), were also compared with the values obtained from two popular integral equations, the Coats–Redfern (CR) [16] and MacCallum–Tanner (MT) [15]. The computation was made using the same theoretical TG data; the results are given in Table 4. It can be seen from this table that eqns. (15) and (16) give E values much closer to the theoretical value than do the other two equations (CR and MT). The deviations of E from the theoretical value are 0.03% and 0.07% respectively for eqns. (15) and (16), and 0.35% and 1% respectively for the Coats–Redfern and MacCallum–Tanner equations.

The validity of the proposed equations was confirmed separately by analysing the theoretical TG data published by Gyulai and Greenhow [6]. Analysis showed that E values obtained from eqns. (15) and (16) are 251.46 and 251.33 kJ mol^{-1} respectively. The theoretical value of $E = 251.16$ kJ mol^{-1} [6] further confirms the validity of the assumptions that we employed here in the derivation of eqns. (15) and (16).

COMPUTATION OF KINETIC PARAMETERS FROM EXPERIMENTAL TG DATA

The new kinetic equations, eqns. (15) and (16), were used to analyse the experimental data for the single-stage dehydration of $ZnC_2O_4 \cdot 2H_2O$ [17], the dehydration of $CaC_2O_4 \cdot H_2O$ and the decomposition of CaC_2O_4 to $CaCO_3$ [18].

TABLE 5

Kinetic parameters from experimental TG data

Kinetic equations	Dehydration of $ZnC_2O_4 \cdot 2H_2O$			Dehydration of $CaC_2O_4 \cdot H_2O$			Decomposition of CaC_2O_4		
	E	*A*	*r*	*E*	*A*	*r*	*E*	*A*	*r*
Equation (15)	107.4	4.737×10^{10}	0.9990	107.0	8.638×10^{10}	0.9986	253.9	3.943×10^{15}	0.9995
Equation (16)	107.3	3.683×10^{10}	0.9990	106.9	6.787×10^{10}	0.9985	253.5	2.858×10^{15}	0.9996
Coats–Redfern	106.3	5.184×10^{10}	0.9990	106.8	3.757×10^{10}	0.9983	250.9	1.040×10^{15}	0.9995
McCallum–Tanner	109.8	5.858×10^{10}	0.9992	106.1	2.796×10^{10}	0.9985	256.5	3.491×10^{15}	0.9995

E in kJ mol^{-1} and *A* in s^{-1}.

The kinetic parameters calculated using eqns. (15) and (16) and with the Coats–Redfern and MacCallum–Tanner equations are given in Table 5. The same good agreement as is observed in the case of the theoretical TG data is shown. Thus, analysis of theoretical and experimental TG data indicates that the two equations derived in this work have equal or better applicability for the computation of kinetic parameters from non-isothermal processes.

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