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New Equations for Kinetic Analysis of Non-isothermal Thermogravimetry

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New equations have been proposed for the evaluation of the kinetic parameters from non-isothermal thermogravimetry. The Arrhenius temperature integral, ln p(x), values were computed from the recently proposed series and approximations. The validity of the new equations has been confirmed by the analysis of theoretical and experimental thermogravimetric curves. The kinetic parameters computed using the proposed equations show better agreement for theoretical TG curves than the well-known methods.

Key Words: Non-isothermal thermogravimetry, Kinetic analysis, Activation energy.

INTRODUCTION

Non-isothermal methods have been extensively used for the study of the kinetics and mechanism of condensed phase reactions[1]. In general, most methods of kinetic analysis of thermoanalytical data begin with the Arrhenius' equation,

$$k = A \exp(-E/RT) \tag{1}$$

and a rate expression

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

In first equation, E, T, R, A and k are the energy of apparent activation (kJ mol^{-1}), absolute temperature, gas constant in kJ/mol, Arrhenius factor and specific rate constant, respectively. In eqn. 2, $f(\alpha)$ is a so-called kinetic function that depends on the reaction mechanism, where α represents the fractional conversion (increasing from 0 to 1) in the solid reactant during the course of the reaction. With a constant temperature increase, $dT/dt = \beta$, (β is the heating rate in ºC/min) integration of eqn. 2 leads to

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$$\int_0^{\alpha}[\frac{1}{f(\alpha)}]d\alpha=\frac{AE}{R\beta}p(x)\,(x = -E/RT) \tag{3}$$

where p(x) is an exponential function of temperature and has no closed-form solution. The left-hand side of this equation is known as the conversion integral g(α) and can be derived for each f(α) used.

From the logarithmic form of eqn. 3

$$\ln g(\alpha) - \ln p(x) = \ln\frac{AE}{R\beta} \tag{4}$$

is obtained.

It is readily seen that the right-hand side is dependent of temperature, while the left-hand side is temperature independent. There are many series expansions for p(x), which has either a series solution or a numerical integral solution. Because the Arrhenius temperature integral and p(x) or p(E/RT) have no closed-form solutions, Schlömilch series[2] and asymptotic expansions[3] given in Table-1, are the most important.

New approximations

We propose two new series approximation for the Lagrange interpolation[4].

Elements of base for Lagrange interpolation: x(x-1) for [-1,1]
x(x-1)(x+1) for [-2,1]
x(x-1)(x+1)(x+2) for [-3,1]
x(x-1)(x+1)(x+2)(x+3) for [-4,1]
x(x-1)(x+1)(x+2)(x+3)(x+4) for [-5,1]

The first approximation p(x) functions for the approximate values;

$$p(x)=e^{-x}\left[\frac{1}{x(x-1)}-\frac{3}{x(x-1)(x+1)}+\frac{5}{x(x-1)(x+1)(x+2)}-\frac{12}{x(x-1)(x+1)(x+2)(x+3)}+\frac{27.7}{x(x-1)(x+1)(x+2)(x+4)}\right] \tag{5}$$

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x(x-1)(x+1)(x+2) for [-4,1] ¢-3

The second approximation p(x) functions for the approximate values;

$$p(x)= e^{-x}\left[\frac{1}{x(x-1)}-\frac{2}{x(x-1)(x+1)}+\frac{3}{x(x-1)(x+1)(x+2)}-\frac{20.47}{x(x-1)(x+1)(x+2)}\right] \tag{6}$$

The validity of the proposed approximations for p(x) given in eqns. 5 and 6 was tested with reference to the Schlömilch series. A comparison is made with the other approximations given in Table-2. For a typical value of x = 20, % deviation of each proposed approximation from that of the Schlömilch was calculated.

TABLE-1

VARIOUS APPROXIMATIONS FOR THE TEMPERATURE INTEGRAL p(x)

Schlömilch[2]	$p(x)=\frac{e^{-x}}{x(x+1)}\left(1-\frac{1}{(x+2)}+\frac{2}{(x+2)(x+3)}-\frac{4}{(x+2)...(x+4)}+\frac{14}{(x+2)......(x+5)}-....\right)$
Semi-convergent series[3]	$p(x)=\frac{e^{-x}}{x^2}\left(1-\frac{2}{x}+\frac{6}{x^2}-\frac{24}{x^3}+\frac{124}{x^4}-\frac{720}{x^5}....\right)$
Two-term[3]	$p(x)=\frac{e^{-x}}{x^2}\left(\frac{(x+1)}{(x+3)}\right)$
Three-term[5]	$p(x)=\frac{e^{-x}}{x^2}\left(1-\frac{2}{(x+3)}-\frac{5}{(x+1)....(x+3)}\right)$
Series[5]	$p(x)=\frac{e^{-x}}{x^2}\left(1-\frac{2}{(x+3)}-\frac{6}{(x+1)....(x+3)}+\frac{28}{(x+1)...(x+4)}-\frac{120}{(x+1)......(x+5)}+\frac{496}{(x+1)...(x+6)}-....\right)$
Coats and Redfern[6]	$p(x)=\frac{e^{x}}{x^2}(1-\frac{2}{x})$
Zsako[8]	$p(x)=e^{-x}\left(\frac{1}{(x+2)(x-d)}\right)$ where $d=\frac{16}{(x^2-4x+84)}$
Flynn and Wall[9]	$p(x)=\frac{e^{-x}}{x}\left(0.0000035+\frac{0.99871}{x}-\frac{1.9848764}{x^2}+\frac{4.9482092}{x^3}-\frac{11.7850792}{x^4}+....\right)$
Van test[10]	$p(x)=\frac{e^{-x}}{x^2}\left(1-\frac{2}{(x+3)}-\frac{6}{(x+1)....(x+3)}+\frac{30}{(x+1)...(x+4)}-\frac{108}{(x+1)......(x+5)}+\frac{810}{(x+1)...(x+6)}+....\right)$
Senum and Yang[11]	$p(x)=\frac{e^{-x}}{x}\left(\frac{(x^2+10x+18)}{(x^3+12x^2+36x+24)}\right)$
Reich and Stivala[12]	$p(x)=\frac{e^{-x}}{x}\left(\frac{(x+4)}{(x^2+6x+6)}\right)$
Gorbachev[13]	$p(x)=\frac{e^{-x}}{x}\left(\frac{1}{(x+2)}\right)$
Sestak[14]	$p(x)=\frac{e^{x}}{x^2}\left(\frac{674.567-57.412-6.055x^2-x^3}{1699.066+841.655x+49.313x^2-8.022x^3-x^4}\right)$
Doyle approximation[15]	$\log p(x) = -2,315-0,4567x$

TABLE-2
COMPARISON OF ln p(x) FROM DIFFERENT APPROXIMATIONS FOR x = 20

Approximations	-ln p(x)	% deviation from Schlömilch × 10^6
Schlömilch[2]	26.0829514	–
Semi-convergent[3]	26.0830043	202.800
Series[3]	26.0829519	1.900
Three-term[5]	26.0829518	1.500
Two-term[3]	26.0824362	1975.200
Van test[10]	26.0829392	46.800
Senum and Yang[11]	26.0829427	33.300
Reich and Stivala[12]	26.0829797	108.500
Gorbachev[13]	26.0867747	1465.800
Zsako[8]	26.0847926	7059.000
Flynn and Wall[9]	26.0852989	9000.100
First series	26.0829515	0.383
Second series	26.0829476	14.500

(Some of the approximation and series such as Doyle, Sestak and Coats-Redfern approximations, keeping away from value of ln p(x) calculated for x = 20 was not included in table-2) from reference 5

RESULTS AND DISCUSSION

Linearization of the p(x) function and new equations

The p(x) function is a function of E and 1/T, *i.e.*, p(x) = f(E,1/T). According to eqn. 4, since ln p(x) is a logarithm of an exponential function of temperature, then a plot of ln p(x) *vs.* 1/T will be linear. Therefore, ln g(α) must also be a linear function of 1/T. For the correct mechanism, ln g(α) *vs.* 1/T should be a straight line. For other incorrect mechanisms this will not be true. Thus, E and A can be calculated from eqn. 4 in non-isothermal kinetic studies if g(α) and p(x) are known.

It is a fact that, for linear functions E and 1/T depend on ln p(x), individually. Therefore, we have tested their simultaneous dependence on ln p(x) and found that they are, indeed, as seen in Table-2.

The series given in eqns. (5) and (6) for linearization of p(x) was converted to

$$-\ln p(x) = Ax + B \ln x + C$$

A set of linear equations was formed for different values of x (5,20,100) and it was solved analytically. Hence, the following equations for p(x) were obtained.

For the first series solution

$$-\ln p(x) = 0.57663 + 1.8198 \ln x + 1.00272x \quad (7)$$

For the second series solution

$$-\ln p(x) = 2.63145 + 1.0282 \ln x + 1.01855x \tag{8}$$

Substituting in eqn. 4 the above equations for ln p(x)

$$\ln g(\alpha) = \ln\left(\frac{AE}{R\beta}\right) - 0.57663 - 1.8198 \ln x - 1.00272x \tag{9}$$

$$\ln g(\alpha) = \ln\left(\frac{AE}{R\beta}\right) - 2.63145 - 1.0282 \ln x - 1.01855x \tag{10}$$

Substituting x = E/RT and R = 8.314 J mol^{-1} K^{-1} in eqns. 9 and 10, yields the final forms of the kinetic equations.

$$\ln\left(\frac{g(\alpha)}{T^{1.8198}}\right) = \ln\left(\frac{AE}{R\beta}\right) + 3.2776 - 1.8198 \ln E - 0.1206\frac{E}{T} \tag{11}$$

$$\ln\left(\frac{g(\alpha)}{T^{1.0282}}\right) = \ln\left(\frac{AE}{R\beta}\right) + 4.8091 - 1.0282 \ln E - 0.1225\frac{E}{T} \tag{12}$$

The plot of left-hand side of eqns. 11 or 12 *vs.* reciprocal absolute temperature will give linear curves. From here, E and A can be calculated from the slope and intercept, respectively. Eqns. 11 and 12 are similar to the equations proposed by Madhusudanan *et al.*[5], Coats and Redfern[6] and MacCallum and Tanner[7], which are in the form of

$$\ln[g(\alpha)/T^{c''}] = \ln[AE/R\beta] + c' - c'' \ln E - c'''(E/T)$$

Proving the proposed equations using the theoretical data

The proposed equations were tested by theoretical and experimental thermogravimetric data. A theoretical TG curve was generated for activation energy, Arrhenius pre-exponential factor and heating rate that are 100 kJ mol^{-1}, 1.1010 s^{-1} and 10 ºC min^{-1}, respectively. A first-order kinetic equation is formed from eqns. 11 and 12. The above values of E, A and β were substituted in these equations to obtain α-T values. Using these values, activation energies E, correlation coefficients r, were calculated by computer according to eqns. 11 and 12, Coats and Redfern method[6] and series and approximation given by Madhusudanan *et al.*[5] and the results were compared.

The deviations of E from the theoretical value (100 kJ mol^{-1}) are 0.001, 0.303, 0.344 and 0.648 % for first series, Madhusudanan *et al.*[5] (three-term approximation), Madhusudanan *et al.*[5] (series) and Coats-Redfern[6], respectively and 0.008, 0.667, 2.758 and 3.066 % for the second series, Madhusudanan *et al.*[5] (three-term approximation), Madhusudanan *et al.*[5] (series) and Coats-Redfern[6], respectively.

As seen in Table-3, the two series were proposed, especially the first one which give E values much closer to the theoretical data than other two equations (Madhusudanan *et al.*[5] and Coats-Redfern[6]). The correlation coefficients of plots, being 0.9999999999999984 and 0.9999999999999949, respectively and indicating perfect linear fits, support the fact above. Therefore, the proposed series can be used to obtain the kinetic parameters of solid state decomposition reactions.

TABLE-3
COMPARISON OF ACTIVATION ENERGY AND CORRELATION COEFFICIENTS FROM THEORETICAL TG DATA

Equations	E (kJ mol^{-1})	r	% Deviation from theoretical E*
First series	99.999†	0.9999999999999984	0.001
Second series	100.008‡	0.9999999999999949	0.008
Madhusudanan *et al.*[5]	99.697†	0.9999998400000000	0.303
(approximation)	99.333‡	0.9999830000000000	0.667
Madhusudanan *et al.*[5]	99.656†	0.9999997400000000	0.344
(series)	97.242‡	0.9999810000000000	2.758
Coats-Redfern[6]	99.352†	0.9999980000000000	0.648
	96.934‡	0.9999700000000000	3.066

*Theoretical value of E = 100 kJ mol^{-1}.

†E values computed using temperature generated from the first series.

‡E values computed using temperature generated from the second series.

TABLE-4
KINETIC PARAMETERS FROM EXPERIMENTAL TG DATA FOR THE THERMAL DECOMPOSITION OF $Ca_2C_2O_4 \cdot H_2O$
(E in kJ mol^{-1} and A in s^{-1})

Kinetic equations	Reaction I		
	E	A	r
First series	111.99	4.68×10^{10}	0.99924
Second series	113.10	3.21×10^{10}	0.99924
Madhusudanan *et al.*[5] (approximation)	111.80	5.34×10^{10}	0.99923
Madhusudanan *et al.*[5] (series)	111.87	7.20×10^{10}	0.99924
Coats-Redfern[6]	111.62	9.18×10^{10}	0.99923
	Reaction II		
First series	287.20	2.47×10^{17}	0.98998
Second series	290.37	1.31×10^{17}	0.98883
Madhusudanan *et al.*[5] (approximation)	286.69	2.65×10^{17}	0.98878
Madhusudanan *et al.*[5] (series)	294.74	1.50×10^{18}	0.98948
Coats-Redfern[6]	286.20	5.13×10^{17}	0.98868
	Reaction III		
First series	297.34	1.07×10^{13}	0.99161
Second series	299.22	2.80×10^{12}	0.99126
Madhusudanan *et al.*[5] (approximation)	297.00	1.05×10^{13}	0.99125
Madhusudanan *et al.*[5] (series)	297.03	1.08×10^{13}	0.99125
Coats-Redfern[6]	296.64	9.57×10^{12}	0.99121

Application of the proposed equations

In order to test the proposed equations, the kinetic parameters from TG data for the decomposition of calcium oxalate monohydrate were derived and the new kinetic equations, eqns 11 and 12, have been applied successfully to the thermal decomposition of $Ca_2C_2O_4{\cdot}H_2O$. It is well known that calcium oxalate monohydrate decomposes thermally in three stages and the mechanism of decomposition reactions assumed as first order. The activation energy values for each stage as derived from the corresponding TG data are listed in Table-4. The obtained values are compared with the activation energy values derived by other authors[5,8,9].

The results obtained from theoretical and experimental TG data show that the proposed equations are equal or better in comparison to the two integral methods, Madhusudanan *et al.*[5] (three term approximation and series) and Coats-Redfern[6].

Conclusion

We introduce two new series approximation for the computation of the Arrhenius temperature integral, p(x) and suggest two corresponding kinetic equations of the form $\ln[g(\alpha)/T^{c''}] = \ln[AE/\beta R] + c' - c''\ln E - c'''(E/T)$ for the evaluation of apparent kinetic parameters from non-isothermal experiments. Series given in eqns. 5 and 6 was tested with reference to the Schlömilch series, the series that gives closest agreement to the numerically integrated values. The proposed equations (eqn. 11 and 12) were tested by theoretical and experimental thermogravimetric data. The kinetic parameters calculated using eqns. 11 and 12 and with the Coats-Redfern[6] and Madhusudanan *et al.*[5] equations are given in Table-4. The same good agreement as is observed in the case of the theoretical TG data is show. The correlation coefficient of plot for eqn. 11 has been found much better than other two equations. The proposed kinetic equations are in well agreement with the known methods for kinetic analysis of non-isothermal thermogravimetry.

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