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INTEGRATION OF THE RATE CONSTANT AND LINEARIZATION OF THE KINETIC EQUATIONS IN NON-ISOTHERMAL REACTION KINETICS

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ABSTRACT

The theory of reaction rates gives approximations of the type $A\ T^b\ e^{-E/RT}$ for rate constants. In thermal analysis the case where $b = 0$ is used in kinetic calculations. However, if b is regarded as a variable, treatment of the non-isothermal kinetic equations is not more complicated than in the special case of $b = 0$. In this paper Padé approximations, described in the literature of the special functions, and Legendre's continued fractions are proposed for evaluation of the $A\int T^b\ e^{-E/RT}\ dT$ integrals. The Coats–Redfern type methods for the determination of the kinetic parameters are discussed analysing the errors of approximation involved in their deduction. On this basis a modified parameter estimation scheme is proposed.

INTRODUCTION

In thermal analysis the widely used expression for the rate constant (k) is

$$k = A\ e^{-E/RT} \tag{1}$$

Application of eqn. (1) seems to be the most suitable way of describing the overall kinetics of reactions having a complex mechanism. The theory of unimolecular reactions, however, leads to the approximation

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

while in the case of a solid + gas → . . . type bimolecular reaction the expression

$$k = A\ T^{0.5}\ e^{-E/RT} \tag{3}$$

seems to be more correct than eqn. (1). (Here the factor $T^{0.5}$ is connected with the number of gas molecules colliding with the reaction surface in unit time).

In thermoanalytical calculations the simplified eqn. (1) is used when unimolecular decomposition or a solid + gas → . . . type reaction is claimed to be rate determining. Since eqns. (2) and (3) can be well approximated by eqn. (1) in a not too wide range and values of E and A corresponding to eqns. (2) and (3) can be calculated from eqn. (1), the replacement of eqns. (2) and (3) by eqn. (1) is acceptable. But this replacement brings no practical advantages. It can be shown that the application of eqns. (2) and (3) in the non-isothermal kinetics is just as simple (or just as complicated) as that of eqn. (1). It was shown recently by Gorbachev that the same equations, the same approximations and the same parameter estimation methods can be used in all three cases. A similar way will be followed in the present paper, too. Methods described in the literature for the special functions will be proposed for evaluation of the integral

$$\int k \, \mathrm{d}T = \int A \, T^{b} \, \mathrm{e}^{-E/RT} \, \mathrm{d}T \tag{4}$$

These approximations may be useful in theoretical deductions, in kinetic simulation and in graphical or computerized determination of kinetic parameters.

Following the conventions of numerical analysis, the error of the approximations proposed will be estimated by error estimation formulae. As regards the determination of E and A, generalization of the widely used Coats–Redfern type methods will be discussed paying particular attention to improvement of accuracy.

INTEGRATION OF $k(T)$

Introducing the new variable $y = E/RT$ and the notation $s = b + 2$ we have

$$\int_{0}^{T} T^{b} \, \mathrm{e}^{-E/RT} \, \mathrm{d}T = (E/R)^{s-1} \int_{y}^{\infty} y^{-s} \, \mathrm{e}^{-y} \, \mathrm{d}y \tag{5}$$

The integral on the right hand side is denoted by $p_s(y)$

$$p_s(y) \equiv \int_{y}^{\infty} y^{-s} \, \mathrm{e}^{-y} \, \mathrm{d}y \tag{6}$$

,

In ref. 2 Padé approximations are given for this type of integral. The first Padé approximation is

$$p_s(y) \cong y^{1-s} \, \mathrm{e}^{-y} (y + s)^{-1} \tag{7}$$

The equivalent of this formula was also deduced by Gorbachev[1] and by Doyle[3] at $s = 2$.

The second Padé approximation is

$$p_s(y) \cong y^{-s} \, \mathrm{e}^{-y} \, \frac{y + 1}{y + s + 1} \tag{8}$$

In the $s = 2$ case eqn. (8) corresponds to the first term of the series proposed by Van Tets[4].

The Padé approximations of integral (6) are equivalent to the truncated parts of the following continued fractions due to Legendre[2]

$$p_s(y) = \cfrac{y^{1-s}\,e^{-y}}{y + \cfrac{s}{1 + \cfrac{1}{y + \cfrac{s+1}{1 + \cfrac{2}{y + \cfrac{s+2}{1 + \ddots}}}}}} \tag{9}$$

It is not too complicated to estimate the error caused by the truncation of eqn. (9). (Simple differential calculus can be applied regarding the continued fraction as a function of a function of a function . . . etc.). In this way the relative error of eqns. (7) and (8) was found to be approximately

$$\frac{-s}{(y+s)(y+s+1)} \approx -s\,y^{-2} \tag{10}$$

and

$$\frac{s(s+1)}{y(y+s)(y+s+1)} \approx s^2\,y^{-3} \tag{11}$$

respectively.

In thermoanalytical studies y is not less than 10. At $s = 2$ and $y = 10$ the left hand sides of eqns. (10) and (11) are equal to -0.013 and 0.004 respectively. (The actual relative errors of eqns. (7) and (8) are -0.013 and 0.003 at $s = 2$ and $y = 10$). At a more usual y, let us say at $y = 30$, these values are equal to -0.0019 and 0.0002 respectively.

In computer calculations a higher accuracy can be achieved through eqn. (9). Thus if eqn. (9) is truncated at the sixth sign of division, the relative error of the formula will be approximately

$$\frac{-6\,s(s+1)(s+2)}{(y+s)(y+s+1)^2(y+s+2)^2(y+s+3)} \tag{12}$$

At $y = 10$ this expression indicates relative errors of about 10^{-5} at $s = 2$, 2.5 and 3. At $y = 30$ this value is about 10^{-7}.

An alternative way of calculating the $p_s(y)$ integrals is through the application of the following expansion

$$p_s(y) = y^{-s}\,e^{-y}\left(1 + \frac{a_1}{y+1} + \frac{a_2}{(y+1)(y+2)} + \frac{a_3}{(y+1)(y+2)(y+3)} + \ldots\right) \tag{13}$$

This type of series is well known in the literature of thermal analysis from the work of Van Krevelen and coworkers[5] who used the corresponding expansion of $p_1(y)$ given

TABLE 1

COEFFICIENTS FOR EQN. (13)

s	a_1	a_2	a_3	a_4	a_5	a_6
2.0	− 2.0	4.0	− 10.0	30.0	− 108.0	444.0
2.5	− 2.5	6.25	− 18.125	61.563	− 242.656	1088.516
3.0	− 3.0	9.0	− 30.0	114.0	− 492.0	2388.0

by Schlömlich and expressed $p_2(y)$ through $p_1(y)$ by partial integration. However, expansion (13) can be applied directly for $p_2(y)$ as well as for any other $p_s(y)$. The method for determination of the constants a_n can be found in ref. 6. The a_n calculated in this way are given for $s = 2$, 2.5 and 3 in Table 1 for actual kinetic calculations. The relative error of the formula can be estimated by the first omitted term in the series.

Comparison of eqns. (9) and (13) shows that Legendre's continued fractions give more accurate approximations within the same time of computation. (In this comparison eqn. (13) is assumed to be evaluated in a Horner type arrangement to make the calculation faster). A practical advantage of Legendre's method is the lack of the specific coefficient a_n. Thus at proper computer programming the high precision evaluation of any $p_s(y)$ can be carried out by a single program line. However, the choice between eqns. (9) and (13) is a matter of taste.

COATS–REDFERN TYPE LINEARIZATION

At this point evaluation of the kinetic parameters from TG curves will be considered. Let x be the fraction reacted, then the usual kinetic equation of thermal analysis has the form

$$\mathrm{d}x/\mathrm{d}t = k(T)\mathrm{f}(x) \tag{14}$$

where t = time and $k(T)$ = rate constant. Integrating eqn. (14) at constant $\mathrm{d}T/\mathrm{d}t = a$ we have

$$g(x) \equiv \int_0^x \frac{\mathrm{d}x}{f(x)} = \frac{1}{a}\int_{T_0}^{T} k(T)\mathrm{d}T \tag{15}$$

Since usually $k = 0$ at $T < T_0$, T_0 may be regarded as zero. Using eqns. (5) and (6), eqn. (15) can be written in the form

$$g(x) = \frac{A}{a}\left(\frac{E}{R}\right)^{s-1} p_s(y) \tag{16}$$

From eqn. (8) one can see that p_s can be considered as a product of $y^{-s}\,\mathrm{e}^{-y}$ with a factor which changes slowly with y. Let us denote this factor by $q_s(y)$

$$p_s(y) \equiv y^{-s}\,\mathrm{e}^{-y}\,q_s(y) \tag{17}$$

Substituting eqn. (17) in eqn. (16) and remembering that $y = E/RT$ we get

$$g(x) = \frac{AR}{aE}\,T^s\,\mathrm{e}^{-y}\,q_s(y) \tag{18}$$

or in logarithmic form

$$\ln\frac{g(x)}{T^s} = \ln\frac{AR}{aE} + \ln q_s - y \tag{19}$$

If the small term ($\ln q_s$) is neglected a generalization of Coats and Redfern's method[7] is obtained. If ($\ln q_s$) is regarded as constant and is approximated through eqn. (7) then Gorbachev's eqn. (1) is obtained. If higher precision is required, ($\ln q_s$) may be approximated as

$$\ln q_s = c_0 + c_1 y \tag{20}$$

by expanding it in a Taylor series around a point $\bar{y}$. In this way E and A can be evaluated in the following steps:

(1) The values of $\ln g(x)/T^s$ obtained from experimental data x and T are approximated by a linear function of $1/T$

$$\ln\frac{g(x)}{T^s} = B_0 + B_1\frac{1}{T} \tag{21}$$

(2) Using Coats and Redfern's method a first approximation of E is determined through the formula

$$B_1 = -\frac{E}{R} \tag{22}$$

(3) A point $\bar{T}$ is chosen somewhere in the middle of the temperature interval of decomposition and using the first approximation of E the corresponding $\bar{y} = E/R\bar{T}$ is calculated. ($\ln q_s$) is expanded into a Taylor series around this point $\bar{y}$. The corresponding coefficients c_0 and c_1 can be calculated from eqn. (8) which gives the approximation $q_s = (y + 1/(y + s + 1)$. In this way

$$c_1 = \frac{s}{(\bar{y} + 1)\,(\bar{y} + s + 1)} \tag{23}$$

$$c_0 = \ln\frac{\bar{y} + 1}{\bar{y} + s + 1} - c_1\,\bar{y} \tag{24}$$

(4) Knowing the values of c_1 and c_0, E and A can be determined immediately from the equations

$$B_1 = -(1 - c_1)\frac{E}{R} \tag{25}$$

$$B_0 = \ln \frac{AR}{aE} + c_0 \tag{26}$$

(These relations follow directly from eqns. (19), (20) and (21).)

The corrected value of E determined in this way may differ by a few per cent at the most from the value of E provided by Coats and Redfern's or by Gorbachev's method. As regards the values of A, however, the complete omission of the term ($\ln q_s$) may cause an error of up to 50% while neglection of $c_1\bar{y}$ in eqn. (24) may result in an error of 10–30%.

THE ERROR OF LINEARIZATION

In this paragraph deviation of the theoretical $\ln g(x)/T^2$ vs. $1/T$ plots from the perfect straight line will be considered. Using the error formula of the Taylor series we have for the error of linearization

$$\frac{1}{2}\frac{\mathrm{d}^2 \ln q_s(y')}{\mathrm{d}y^2}(y - \bar{y})^2 \tag{27}$$

where y' is an unknown point between y and y'. Approximating q_s through eqn. (8) as above, $\mathrm{d}^2\ln q_s/\mathrm{d}y^2$ is found to be about $-2s/y^3$. If the greatest value of $|y - \bar{y}|$ arising in the given parameter estimation is denoted by Δy, then according to eqn. (19) the $\Delta\ln g(x)/T^2$ corresponding to the Δy is about Δy. The relative error of the linearization is the quotient of expression (27) and $\Delta\ln g(x)/T^2$. In this way it is approximately

$$s\,y^{-3}\,\Delta y \tag{28}$$

Regarding actual values of E and T it can be seen that the term (28) is of the order of 10^{-3} at the most.

OTHER LINEARIZATION TECHNIQUES

Some widely used and well elaborated kinetic evaluation methods[8, 9] are based on the linearity of the $\ln g(x)$ vs. $1/T$ plots. Though at usual values of E and T these plots are fairly linear, it will be shown that the error of linearization is considerable, higher than that of the $\ln g(x)/T^2$ vs. $1/T$ plots and at $y < 20$ this linearization might become deficient in the distinction between the possible mechanism hypotheses It follows from eqns. (16) and (17) that

$$\ln g(x) = \ln \frac{A}{a}\left(\frac{E}{R}\right)^{s-1} - s\ln y + \ln q_s - y \tag{29}$$

Now that the ($-s\ln y + \ln q_s$) function must be linearized, the error term is about

$$\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2}(-s\ln y + \ln q_s)(\Delta y)^2 \approx \left(\frac{1}{2}s\,y^{-2} - s\,y^{-3}\right)(\Delta y)^2 \tag{30}$$

According to eqn. (29) the change of $\ln g(x)$ in a given interval Δy is about

$$\Delta \ln g(x) = \frac{\mathrm{d}}{\mathrm{d}y}(-s \ln y + \ln q_s - y)\,\Delta y \approx -\Delta y \tag{31}$$

In this way the relative error of linearization is approximately

$$(-\tfrac{1}{2} s y^{-2} + s y^{-3})\Delta y \tag{32}$$

Note that eqn. (32) is about y times greater than the term (28). At small y values eqn. (32) indicates errors of about 1%. Since the distinction between different reaction mechanisms is sometimes based on extremely small differences in the correlation coefficients[10], a relative error of 0.5–1% might be important. However, at usual values of y eqn. (32) has sufficiently small values.

The parameter estimation method proposed in the present paper (eqns. (21)–(26)) may be used with the $\ln g(x) = B_0 + B_1\, 1/T$ linearization, too.

The only difference is that eqns. (22), (25) and (26) must be replaced by the following

$$B_1 = -\frac{E}{R} - s \tag{33}$$

$$B_1 = -(1 - c_1)\frac{E}{R} - s \tag{34}$$

$$B_0 = \ln \frac{A}{a}\left(\frac{E}{R}\right)^{s-1} + \ln \bar{y} - 1 + c_0 \tag{35}$$

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