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EVALUATION AND OPTIMIZATION OF INTEGRAL METHODS FOR THE ANALYSIS OF THERMOGRAVIMETRIC DATA

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ABSTRACT

A detailed analysis of the merits and shortcomings of integral methods for the treatment of constant heating rate, non-isothermal kinetic data is presented. A recently developed linearized approach, which is shown to be of the highest accuracy, is used to conduct some of the analyses. From these results generalizations are made concerning the ability to discriminate among alternative mechanisms strictly by the non-isothermal kinetic method.

INTRODUCTION

The analysis of thermogravimetric data for the determination of mechanisms and kinetic parameters has been an area of extensive activity for almost three decades. Integral methods, because of their relative simplicity and their similarities with isothermal kinetics, have received the principal attention. Much of the fundamental mathematical groundwork was described in the early literature [1–7] and has already been comprehensively reviewed [8]. Yet, a steady flow of refined formulations and computational schemes continues. Šesták has warned that such refinements are probably not as essential as the establishment of a secure mechanistic framework for solid-state reactions [9]. Such a recommendation is certainly justified, although it presumes that the book is essentially closed on how the data might best be analyzed. There are several reasons which indicate that this is not the case.

First, little has been done in an analytical fashion to evaluate the relative accuracy with which A, the pre-exponential factor, and E, the activation energy of the Arrhenius rate constant, can be determined by each of the proposed integral methods. Aside from a noteworthy attempt by Broido and Williams [10] most of the evaluations have been empirical and have therefore lacked generality. To counter the criticism that the available accuracy is already within the limits of the experimental variations, one must remember that calculational error only serves to compound the uncertainty in the final

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results. Secondly, the rate parameters determined by each of the various methods are specific to the method used to derive them. Thus, if they are not determined to high accuracy, they can only be used to estimate extents of reaction through the same approximate expressions from which they evolved. This is a highly undesirable situation, unlike that in isothermal kinetics where a given mechanism, along with the rate parameters, uniquely determines reaction history. It would be advantageous if the body of data and analysis which has grown in non-isothermal kinetics could be meaningfully compared on a standard and absolute basis. Finally, a question which receives frequent attention is what the limits of calculational methods might be in discriminating among alternative mechanisms for a given reaction. Are there firm limits on what information can be extracted from a non-isothermal experiment, or are we separated by just another mathematical adjustment from learning more than we could previously? Again, some answers have been provided empirically but little generalization has found its way into the fundamentals of the subject.

The aim of this report is to address, and in most cases definitively resolve, all of these issues. Since there are but a few fundamentally different mathematical treatments of the integral method commonly referred to, we will begin with a review, giving detailed attention to the assumptions involved in their development and the resulting limitations on their accuracy and applicability. Similar treatment will then be given to a new approach for a high-accuracy solution to the integral problem which is graphable and has a simple and convenient functional form. Finally, its relationship to previous methods, and an exacting comparison of accuracy and utility, will be given. The result will be not only a new graphical method of unsurpassed accuracy but also a more comprehensive understanding of what may reasonably be expected of the integral method in general.

BACKGROUND

The integral form for analysis of non-isothermal kinetic data obtained at constant heating rate ϕ is given by

$$g(\alpha) = \frac{A}{\phi} \int_0^T e^{-E/RT} \, dT \qquad (1)$$

where $g(\alpha)$ contains the mechanistic relation for the extent of reaction α. The objectives of a kinetic study are to determine the most appropriate mechanism and to evaluate the associated energy parameter, E, as well as the pre-exponential factor, A. These tasks are made difficult by the fact that the integral cannot be solved exactly. However, a simple integration by parts converts the Arrhenius integral into a function of the exponential integral, which can be evaluated to any desired degree of accuracy using either special numerical approximations [11], the rational or Schlömilch approximations [7,12,13], or asymptotic expansions [2,4–6,10]. Given values of A and E it is straightforward to generate numerical values for $g(\alpha)$, and conversely given $g(\alpha)$ as a function of temperature one can in principle extract best-fit values for E and A. The latter process is quite tedious, however, requiring iterative numerical computation, and also uninformative since it obscures any functional relationships which might lead to generalizations. For these reasons simplified approximations to the integral have been sought which provide representative values of E and A.

The desired approximation would have the linear form

$$\ln g(\alpha) = \ln R + S\theta(T) \tag{2}$$

where R and S are constants and $\theta(T)$ is a simple function of temperature. If only R contains the pre-exponential factor, and if S contains the activation energy, then the slope and intercept of the line determine the rate parameters simply. The earliest approaches involved expansions of $1/T$ in the integrand of eqn. (1) to create integrable functions. Van Krevelen et al. [1] used

$$\frac{1}{T} = \frac{1}{T_r}\left[1 - \left(\frac{T - T_r}{T_r}\right) + \ldots\right] \tag{3}$$

and Horowitz and Metzger [4] used

$$\frac{1}{T} = \frac{1}{T_r}\left[1 - \ln\left(\frac{T}{T_r}\right) + \ldots\right] \tag{4}$$

where T_r is an arbitrarily defined reference temperature. If the reference temperature is selected to be within the temperature extremes of the experiment, then both expansions are quite accurate in any realistic situation. Van Krevelen's solution is written

$$g(\alpha) = \frac{A}{\phi}\,\frac{eT_r}{E/RT_r + 1}\left(\frac{T}{eT_r}\right)^{E/RT_r + 1} \tag{5}$$

where $S = E/RT_r + 1$ and $\theta(T) = \ln T$, using the notation of eqn. (2). Horowitz and Metzger's solution is written

$$g(\alpha) = \frac{A}{\phi}\,\frac{RT_r^2}{E}\,e^{-2E/RT_r}\,e^{ET/RT_r^2} \tag{6}$$

where $S = E/RT_r^2$ and $\theta(T) = T$.

Neither of these formulations is any longer in much use and there are two predominant reasons for their failure. The first concerns the arbitrary nature of the reference temperature selection. It was sensibly desired that it be a reference point which would be recognizable by any investigator. The temperature at which the reaction rate was a maximum was apparently selected on the intuitive justification that the proper link between the mathematics and the experiment should be related to the point at which most of the reaction occurs. While certainly reasonable, it is no less arbitrary from an analytical standpoint. The proper reference temperature is crucial for accuracy, however, since the activation energies calculated from the slopes of logarithmic plots of eqns. (5) and (6) are multiplicative factors of the reference temperature and its square, respectively. Improper selection of T_r thus results in equivalent or larger errors in the evaluation of E. Little effort to optimize the reference temperature can be found in the literature. We will see that not only can this be achieved analytically, but also that the common selection of temperature at maximum reaction rate was seriously in error. The purpose is not to revive these approaches but rather to illustrate the value of the optimization process.

The second reason these older approaches were unsuccessful was discussed by Broido and Williams [10]. By asymptotic expansion of the Arrhenius integral they demonstrated that the functional form of the Horowitz and Metzger solution, $\theta(T) = T$, was a poor approximation to the actual function. The Van Krevelen solution, with $\theta(T) = \ln T$, was certainly better, but it could be shown that $\theta(T) = 1/T$ would be most representative of the actual temperature dependence of the integral. Horowitz and Metzger proposed such a solution [5], with $S = -E/R$, completely independent of the reference temperature. Unfortunately, while the correlation coefficients were much higher than those of the previous methods, the error in the activation energy still ran as high as 10% at $E/RT \approx 20$ and 5% at $E/RT \approx 40$. Again, Broido and Williams demonstrated that the error in evaluating the activation energy from this model would go as $2RT_r/E$ and suggested that the value of E obtained from the slope of a $\ln g(\alpha)$ vs. $1/T$ plot be diminished by $2RT_r$, where T_r was loosely defined as "an arbitrarily selected temperature in the experimental range" [10]. Since the error produced in E now depends additively rather than multiplicatively on the reference temperature, the absolute value of T_r is not as critical to the accuracy of the energy, but still must be carefully selected to reproduce A correctly. Little has been done to pursue this reasoning, although we shall see that the suggestion leads to the most accurate solution available.

The technique which has been used most commonly is based on expansions of the Arrhenius integral, either the asymptotic expansion usually attributed to Coats and Redfern [6]

$$g(\alpha) = \frac{A}{\phi}\frac{RT^2}{E}\left[1 - \frac{2RT}{E}\right] e^{-E/RT} \tag{7}$$

or the similar Schlömilch expansion

$$g(\alpha) = \frac{A}{\phi}\frac{RT^2}{E}\left[1 + \frac{2RT}{E}\right]^{-1} e^{-E/RT} \tag{8}$$

For large values of E/RT, eqns. (7) and (8) are essentially identical. If one assumes that only the exponential term varies significantly over the temperature range of interest, then both expressions reduce to the second Horowitz and Metzger solution, which we have just discussed and shown to be of low accuracy. Useful versions of these equations, obtained by assuming that only the bracketed terms are constant over the temperature range and may be set equal to unity, are

$$\ln g(\alpha) - 2 \ln T = \ln\left(\frac{A}{\phi}\frac{R}{E}\right) - \frac{E}{RT} \tag{9}$$

Equation (9) gives extremely high correlation coefficients and reproduces values of E with great accuracy. This formulation has stood out as the simplest and most accurate method for treating thermogravimetric data. However, because of the approximation in eliminating the bracketed terms the values of A obtained are seriously in error, particularly as E/RT gets smaller. No analytical method has been offered to correct this and, as a result, the values of A and E do not satisfactorily regenerate the original data when used in a high-accuracy numerical approximation. Also, the functional form of eqn. (9) is sufficiently different from that of eqn. (2) as to make generalizations about the sensitivity to different mechanisms difficult.

In summary, eqn. (9) has been the most useful and accurate approximation developed for thermogravimetric analysis to date. In order to demonstrate a more accurate and general purpose solution we will now return to the subject of optimization of the reference temperature used in solutions based on expansions of T about T_r.

THEORETICAL

It has recently been shown, using eqn. (4), that eqn. (1) can be made integrable to yield a graphable solution with $\theta(T) = 1/T$ [14]. Rewriting eqn. (4) we obtain

$$\left[\frac{T_r}{T}e^{1-T_r/T}\right]^2 \approx 1 \tag{10}$$

Substituting this directly in eqn. (1) as a simple multiplier of the integrand results in the integrated form

$$g(\alpha) = \frac{A}{\phi}\frac{e^2 T_r^2}{E/R + 2T_r}e^{-(E/R+2T_r)/T} \tag{11}$$

Note that using eqn. (10) as a multiplier, rather than within the exponential term, makes the integral much less sensitive to errors induced by the approximation than the previous approaches have been. Also, the values of E are fairly insensitive to the selection of T_r since it is merely an additive constant in the slope of the ln g(α) vs. $1/T$ line. Finally, it is important that the value of the additive constant is precisely what was recommended by Broido and Williams as a result of their analysis of linearized treatments [10]. It should be noted that eqn. (11) can also be simply derived from eqn. (8) (shown by Doyle [7] to be more accurate than eqn. (7)) by substitution of eqn. (10) in all terms except the exponential and assuming that the bracketed term is essentially constant.

Once again, in order to make eqn. (11) of high utility it is necessary to optimize the selection of the reference temperature. This is not a straightforward task and we will approach it in two steps. Figure 1 illustrates a comparison of the logarithm of the actual Arrhenius integral with a straight-line fit. The slight curvature of the Arrhenius integral has been exaggerated for clarity. We first ask whether we can define the temperature at which the function has the same slope as the best-fitted line. This question is a major hurdle in addressing the optimization issue and was answered by demonstrating that the geometric mean of the temperature extremes of the plot, $T_g = (T_1 T_2)^{1/2}$, is, to high accuracy, the temperature which approximates the point at which the slopes are equal. The approach for this proof was given by Kassman and Squire [15] and will not be repeated here. It can be shown that this relationship holds for any reasonable temperature range which occurs in practice. Also, it will be of interest to know that the same result applies if the analysis is carried out with $\theta(T) = \ln T$ and $\theta(T) = T$, the functional forms due to Van Krevelen, and Horowitz and Metzger.

Having a unique point at which to evaluate the slope of a fitted line to the Arrhenius integral, which is independent of any details of an experiment

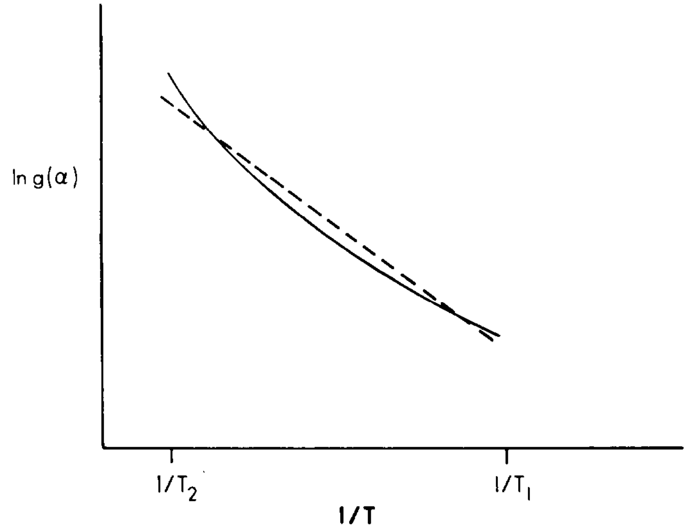

Fig. 1. Representation of the relationship between the Arrhenius integral (———) and the linear approximation (- - - - - -).

other than the temperature extremes, makes the evaluation of the reference temperature both simple and accurate. As an example, we take eqn. (8) as a first approximation to the Arrhenius integral. If we equate the logarithmic forms of eqns. (8) and (11) we obtain

$$\ln\left[\frac{A}{\phi}\frac{e^2T_r^2}{E/R+2T_r}\right]-\frac{E/R+2T_r}{T}=\ln\frac{A}{\phi}+\ln T-\frac{E}{RT}-\ln\left[\frac{E}{RT}+2\right] \tag{12}$$

Then, taking the derivatives of both sides with respect to $1/T$ and evaluating the right-hand side at T_g yields

$$E/R+2T_r=T_g+E/R+\frac{E/R}{E/RT_g+2} \tag{13}$$

where the left-hand side is the negative slope of the fitted line, which we will call S, and the right-hand side is the negative slope of the approximate Arrhenius integral. Since $S=E/R+2T_r\approx E/R+2T_g$, we can make the appropriate substitutions in the right-hand side to give

$$T_r=T_g\left[1-\frac{T_g}{S}\right] \tag{14}$$

Thus, as a first approximation, eqn. (14) gives the reference temperature as a simple function of T_g and the observed slope of the fitted line.

For even higher accuracy we can repeat this process using higher order rational approximations to the Arrhenius integral [13], however it is readily shown that the next order term is sufficient to establish the accuracy of T_r for all practical situations. The result is

$$T_r=T_g\left[1-\frac{T_g}{S}+\frac{2T_g^2}{S^2}\right] \tag{15}$$

Because eqn. (11) has a functional form which is similar to that of the rational approximations, this derivation of T_r is relatively straightforward. If one were to attempt the same optimization for the Van Krevelen or Horowitz and Metzger solutions, the functional forms of the expressions for T_r that would result would be somewhat more cumbersome than eqn. (15). Nevertheless, the remarkable result is that the numerical values obtained for the optimum reference temperature for all the methods are, for all practical purposes, identical! Let us see how this affects the accuracy of the various approximations.

RESULTS AND DISCUSSION

Table 1 contains comparisons of the calculated values of A and E for the four approximations given by the present method (eqn. 11), the Coats and

Redfern technique (eqn. 9), and the Van Krevelen, and Horowitz and Metzger approximations (eqns. 5 and 6, respectively). Values of ln g(α) have been generated using a high-accuracy rational approximation (third degree [13]) and constant values of $A/\phi = 1$ and $E/R = 10{,}000$, over five temperature intervals. These values of ln g(α) have then been used at ten equally spaced temperatures in each range to calculate slopes and intercepts. T_{r} was calculated using the present method (eqn. 15) and the same reference temperature was used in the A and E calculations for all but the Coats and Redfern approach, which contains no reference temperature. The temperature ranges span a range of E/RT values from 12 to slightly over 46. The first column contains the calculated values of the current method along with the reference temperature. It is obvious that the accuracy of both the A and E values is quite impressive. The accuracy of the E values by the Coats and Redfern method is also quite adequate, but note that the A values falter with decreasing E/RT, in direct relation to the error introduced by ignoring the bracketed term of eqn. (7). The last two columns are most surprising. Using the optimized reference temperature we see that the E values determined by both of the older methods are quite good. In fact, use of the optimized reference temperature results in the method of Van Krevelen being of comparable accuracy with that of Coats and Redfern. As noted earlier, asymptotic expansions of $1/T$ in the exponential term magnify the errors of these approximations, and thus the Van Krevelen, and Horowitz and Metzger methods become more accurate at the lower values of E/RT where the exponential term itself spans a smaller range of values.

Although it has been shown that the older techniques can be vastly improved by optimizing the reference temperature, at least in regard to the

TABLE 1

Fitted values of the rate parameters

Temp. range (K)	Present method (eqn. 11)		Coats–Redfern (eqn. 9)		Van Krevelen (eqn. 5)		Horowitz–Metzger (eqn. 6)	
	A/ϕ	E/R	A/ϕ	E/R	A/ϕ	E/R	A/ϕ	E/R
215–296	1.0030 $T_{\mathrm{r}} = 246.5$	9998	0.9088	9988	0.8782	10022	0.5195	9948
296–395	1.0025 $T_{\mathrm{r}} = 331.7$	9998	0.8806	9979	0.9372	10025	0.7004	9977
395–512	1.0021 $\mathrm{T}_{\mathrm{r}} = 432.6$	9998	0.8490	9965	0.9715	10029	0.8337	10007
512–656	1.0018 $T_{\mathrm{r}} = 552.4$	9997	0.8139	9945	0.9954	10040	0.9219	10046
656–818	1.0010 $T_{\mathrm{r}} = 691.4$	9995	0.7760	9916	1.0210	10057	1.0180	10104

accuracy with which they determine A and E, they still have serious shortcomings. As discussed earlier, Broido and Williams found these functional forms not to be optimum in simulating the temperature-dependence of the Arrhenius integral. Even though A and E are individually fairly accurate, together they misrepresent the data from which they were calculated. This is shown in Table 2, where comparisons are made with respect to original data. In the first column are shown values of α generated by a high-accuracy rational approximation for a first-order chemical reaction using $A/\phi = 5 \times 10^7$ and $E/R = 10{,}000$, for the middle range of temperatures of Table 1. In the same order of presentation, each technique is used to regenerate α from the calculated values of A/ϕ (multiplied by 5×10^7), E/R, and T_r using the same high-accuracy rational approximation. We now see that the present method reproduces each value of α to within 1%. The Coats and Redfern technique has produced values of A and E which misrepresent α by as much as 10%. It is apparent from the last two columns that even high-accuracy values of A and E can easily misrepresent original values of α because they are paired badly during fitting. However, their improvement in accuracy in determining values of A and E is not surprising since the optimized reference temperature is separated from the temperature of maximum reaction by at least 40 K, reducing what previously would have been a 10% error in reference temperature to virtually nothing.

The final point to be discussed is the ability with which different mechanisms can be discriminated by analyzing the data of a single non-isothermal kinetics experiment. We must now accept that the functional form of eqn. (2), as expressed by our solution in eqn. (11), is an extremely accurate, linearized version of the Arrhenius integral, and can be used functionally in its place. From Tables 1 and 2 we can safely say that it reproduces all the parameters within their limits of measurability. Let us now examine the case

TABLE 2

Recalculated extents of reaction, α

T (K)	Exact	Present method	Coats–Redfern	Van Krevelen	Horowitz–Metzger
395	0.731E-2	0.736E-2	0.680E-2	0.658E-2	0.599E-2
408	0.173E-1	0.175E-1	0.161E-1	0.157E-1	0.142E-1
421	0.388E-1	0.391E-1	0.360E-1	0.352E-1	0.319E-1
434	0.820E-1	0.826E-1	0.760E-1	0.746E-1	0.677E-1
447	0.162	0.163	0.150	0.148	0.135
460	0.297	0.298	0.276	0.274	0.251
473	0.491	0.493	0.462	0.459	0.425
486	0.714	0.716	0.682	0.681	0.642
499	0.895	0.896	0.872	0.872	0.843
512	0.980	0.981	0.972	0.973	0.960

of a mechanism, $h(\alpha)$, which is related to another mechanism, $g(\alpha)$, by

$$h(\alpha) = a[g(\alpha)]^n \tag{16}$$

where a and n are arbitrary constants. Then, as before

$$\ln h(\alpha) = \ln a + n \ln g(\alpha) = \ln R + S/T \tag{17}$$

But we also have from eqn. (17)

$$\ln g(\alpha) = [\ln(R/a) + S/T]/n \tag{18}$$

Thus both mechanisms would fit equally well, with the slopes being related by the factor n. Criado and Morales [16,17] predicted a similar result on the basis of eqn. (9), from which the conclusion can only be weakly drawn. It also was erroneously concluded that the calculated activation energies would be directly related by the factor n, rather than the slopes as given by $E/R + 2T_r$. Attempts have been made in the literature [18] to provide alternative analyses of data sets which would circumvent the results implied by eqns. (17) and (18). Closer inspection of these analyses will reveal that differences in the quality of fit are merely related to the weighting factor n, and that no more information has really been made available.

We can now, within the limits of sensible experimental practice, make some generalizations about the distinguishability of mechanisms from a single non-isothermal data set. All the power law expressions, $g(\alpha) = \alpha^{1/n}$, are indistinguishable from each other and from the one-dimensional diffusion mechanism, $g(\alpha) = \alpha^2$. The nucleation and growth (Avrami–Erofeev) mechanisms, $g(\alpha) = [-\ln(1-\alpha)]^{1/n}$, are indistinguishable from each other and from a simple first-order chemical reaction. The contracting volume mechanism, $g(\alpha) = 1 - (1-\alpha)^{1/3}$, is indistinguishable from the three-dimensional diffusion (Jander) mechanism, given as its square. Criado and Morales [17] also attempted to show that the two-dimensional diffusion model, $g(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha$, cannot be distinguished from the contracting-area mechanism, $g(\alpha) = 1 - (1-\alpha)^{1/2}$, and that the three-dimensional diffusion (cylindrical) mechanism, $g(\alpha) = (1 - 2\alpha/3) - (1-\alpha)^{2/3}$, also cannot be distinguished from the contracting-volume model. These results were based on empirical analyses of a limited range of extents of reaction, and do not hold in general. The mechanisms compared by Criado and Morales are distinguishable, at least in principle.

CONCLUSIONS

As promised at the outset, several questions have been answered unambiguously. First, it has been shown that a linearized approximation to the Arrhenius integral (eqn. 11) can be used to evaluate the rate parameters of the Arrhenius rate constant with exceptional accuracy. The approximation is enhanced by optimizing the selection of the reference temperature, which is based solely on the initial and final temperatures of the experiment and the slope of the fitted line. It was also shown that similar optimization could be applied to the Van Krevelen, and Horowitz and Metzger approaches, yielding improved but still lower accuracy. The present approach was also shown to be superior to the method of Coats and Redfern. Using a high-accuracy, rational approximation, it was demonstrated that the values of A and E evaluated by the present method reproduce the original data with notably higher accuracy than any other available method. Finally, the high accuracy of the new approach allowed its functional form to be used in setting definitive limits on the ability to discriminate alternative mechanisms.

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