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AN ACCURATE AND GRAPHABLE SOLUTION FOR THE INTEGRAL OF THE ARRHENIUS FUNCTION

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ABSTRACT

An approximation to the integral of the Arrhenius function is found by incorporating a nearly-constant integrating factor. The solutions, which can be determined graphically, are of an accuracy comparable to that of the rational approximations.

INTRODUCTION

The general kinetic equation for non-isothermal investigations

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

remains the subject of many efforts to obtain solutions of high accuracy and relative simplicity. Numerous approximations to the integral of the Arrhenius function [1—4] have been demonstrated, each having a high degree of accuracy but requiring computer-assisted, non-linear curve-fitting techniques. Two noteworthy attempts at providing solutions which can be graphed [5,6] with comparable simplicity to isothermal kinetic systems have long been abandoned because of the inherent errors introduced by the approximations on which they are based. An approximate solution will be discussed here which can be readily graphed or evaluated by a linear least-squares method, and yields activation energies and Arrhenius factors of an accuracy comparable to that of the rational approximations.

DISCUSSION

It has been shown [7] that a near-constant integrating factor for the Arrhenius integral is provided by the approximation

$$\left[\frac{T_i}{T} e^{1-T_i/T}\right]^2 \cong 1 \tag{2}$$

where T_i is a constant whose evaluation will be discussed in detail later. Substitution into eqn. (1) results in the integrated form

$$g(\alpha) = \frac{A}{\phi}\frac{e^2T_i^2}{E/R + 2T_i}\, e^{-(E/R+2T_i)/T} \tag{3}$$

and a plot of ln g(α) vs. $1/T$ is linear with negative slope $E/R + 2T_i$. The prior methods developed by Van Krevelen et al. [5] and Horowitz and Metzger [6] were based on expansions of the integrand of eqn. (1) about $T = T_i$ and resulted in the solutions

$$g(\alpha) = \frac{A}{\phi}\frac{eT_i^2}{E/R + T_i}\left(\frac{T}{eT_i}\right)^{E/RT_i+1} \tag{4}$$

and

$$g(\alpha) = \frac{A}{\phi}\frac{RT_i^2}{E}\, e^{-2E/RT_i}\, e^{ET/RT_i^2} \tag{5}$$

respectively. In these two cases T_i has usually been selected as the inflection point in the α—T curve, thereby being determined by the experimental data. Regardless of how T_i is selected, the sensitivity of the calculated activation energy and Arrhenius factor to T_i in eqns. (3)—(5) can be evaluated and the results are tabulated in Table 1.

Considering that the value of T_i will usually be within the limits of the temperature range of the experiment, it is obvious that the methods of Van Krevelen and Horowitz and Metzger are extremely sensitive to the proper selection of T_i, and that for $E/RT_i > 5$ they would be of questionable value for evaluating the Arrhenius factor. Since it can be shown that the inflection point is not the optimum temperature for the assignment of T_i, activation energies calculated from eqns. (4) and (5) were also frequently in considerable error. Unfortunately, the awkward functional forms of these prior approximations do not lend themselves to formulation of proper criteria for the selection of the best temperature constant. The approximation described here allows the Arrhenius factor to be calculated with the same accuracy that the prior methods had for the activation energies, and for $E/RT_i > 5$ the activation energy can now be calculated to high accuracy almost independently of the value of T_i.

A significant advantage of eqn. (3) is that its functional form is quite similar to those of the rational approximations. This similarity can be used beneficially, with moderate effort, to devise an analytic relationship for the eval-

TABLE 1

Relative errors in calculation of A and E

	$d \ln A/dT_i \times 100$ (%)	$d \ln E/dT_i \times 100$ (%)
Present approximation	$200/T_i$	$(200/T_i)/(E/RT_i)$
Van Krevelen et al. [5]	$(100/T_i)\,(E/RT_i)$	$100/T_i$
Horowitz and Metzger [6]	$(200/T_i)\,(E/RT_i)$	$200/T_i$

uation of T_i. Such a meaningful selection of T_i renders the present approximation of comparable accuracy with the rational approximations, as will be demonstrated.

For illustrative purposes we will use the Gorbachev (or first-order rational) approximation [4] as a true representation of the Arrhenius integral.

$$\frac{A}{\phi}\int e^{-E/RT}\,dT \cong \frac{A}{\phi}\frac{T^2\,e^{-E/RT}}{E/R + 2T} \tag{6}$$

Figure 1 illustrates the relationship between eqn. (6) and eqn. (3) in a logarithmic plot. Within the range T_1 to T_2 a unique temperature T_* exists at which the slope of the experimental data is the same as the slope of the fitted straight line. Equating the first derivatives with respect to the inverse temperature of the logarithmic forms of eqns. (3) and (6) one obtains

$$S \equiv \frac{E}{R} + 2T_i = \frac{E}{R} + T_* + \frac{E/R}{E/RT_* + 2} \tag{7}$$

Rearranging and solving for T_i yields

$$T_i = T_*\left[1 - \frac{T_*}{E/R + 2T_*}\right] \tag{8}$$

Finally, introducing the slope S from the left-hand side of eqn. (7) to eliminate E/R, and making the assumption that the difference $T_* - T_i$ is negligible compared to the magnitude of the slope, we arrive at the following condition

$$T_i = T_*\left[1 - \frac{T_*}{S}\right] \tag{9}$$

If instead higher order rational approximations are used to relate T_i to T_* then additional terms are added in an alternating series to the right-hand side of eqn. (9). For the accuracy desired, the following equation contains all essential terms

$$T_i = T_*\left[1 - \frac{T_*}{S} + 2\frac{T_*^2}{S^2}\right] \tag{10}$$

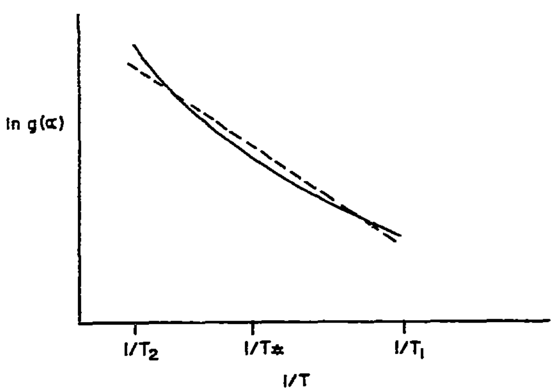

Fig. 1. Representation of the relationship between the Arrhenius integral (———) and the linear approximation (— — —).

It remains to be shown that in any temperature range a value of T_* can be assigned which is independent of the details of the experiment and is a function only of the end points of the temperature range. A general expression for the assignment of T_* is not readily found. One can, for example, represent the logarithm of the Arrhenius integral to great accuracy by a function of the form

$$\ln g(\alpha) = a + \frac{b}{T} + \frac{c}{T^{1/2}} \tag{11}$$

where a, b, and c are fitting constants. In the interval T_1 to T_2 a straight-line fit to this function gives, independently of a, b, and c

$$T_* = (T_1 T_2)^{1/2} \left[1 - \tfrac{7}{80}\left(\frac{T_2 - T_1}{T_1}\right)^2 + \ldots\right] \tag{12}$$

For $T_2 < 1.4T_1$, T_* differs from the geometric mean of the end points of the temperature range by less than 1%. Alternative representations to eqn. (11) support the conclusion that T_* is adequately given by the geometric mean, T_g. Equation (10) can then be rewritten

$$T_i = T_g \left[1 - \frac{T_g}{S} + 2\frac{T_g^2}{S^2}\right] \tag{13}$$

Rewriting eqn. (3) in logarithmic form

$$\ln g(\alpha) = \ln\left[\frac{A}{\phi}\frac{e^2 T_i^2}{E/R + 2T_i}\right] - \frac{E/R + 2T_i}{T} \tag{14}$$

A plot of $\ln g(\alpha)$ against $1/T$ gives a line of negative slope $E/R + 2T_i$. Substitution of eqn. (13) for T_i allows evaluation of E/R from the slope and A/Φ from the intercept. Table 2 demonstrates the accuracy of the application of eqn. (14) to a series of hypothetical TGA curves. The function $g(\alpha)$ has been generated [8] at intervals of 10° over the temperature ranges shown. The ranges were selected to simulate observable extents of reaction for first-order kinetic schemes. In the vicinity of $E/RT \cong 5$ the approximation yields an Arrhenius factor and activation energy within 1% of the actual values, and for $E/RT > 5$ the agreement is comparable to that which could be achieved using any rational approximation.

TABLE 2

Comparison of linear approximation with generated kinetic data

Generation parameters				E/RT	Fitted values	
T_1 (K)	T_2 (K)	A/Φ	E/R		A/Φ	E/R
180	350	5.000	1500	4.3— 8.3	5.007	1490
310	430	13 000	5000	11.6—16.1	13 040	4997
650	810	1.000×10^7	15 000	18.5—23.1	1.002×10^7	14 997

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REFERENCES

1 A.W. Coates and J.P. Redfern, Nature (London), 201 (1964) 68.
2 B. Carrol and E. Manche, Thermochim. Acta, 3 (1972) 449.
3 V.M. Gorbachev, J. Therm. Anal., 8 (1975) 349.
4 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.
5 D.W. Van Krevelen, C. Van Herden and F.J. Huntjens, Fuel, 30 (1951) 253.
6 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
7 A.J. Kassman, J. Therm. Anal., 18 (1980) 118.
8 M. Abramowitz and I.A. Stegun (Eds.), Handbook of Mathematical Functions, National Bureau of Standards, Washington, D.C., 1964.