Short communication

RATIONAL APPROXIMATIONS OF THE INTEGRAL OF THE ARRHENIUS FUNCTION

G. I. SENUM and R. T. YANG

Department of Applied Science Brookhaven National Laboratory Upton, New York 11973 U.S.A

(Received September 25, 1976)

Rational approximations have been derived for the integral of the Arrhenius function $\int_0^T \exp(-E/RT)\,dT$ which is important in the kinetic analysis of thermogravimetric data. The first degree rational approximation is found to be equivalent to the Gorbachev approximation, i.e., $RT^2 \exp(-E/RT)/(E+2RT)$. The second degree rational approximation is more accurate than the Zsakó empirical approximation when $E/RT < 1$ and $E/RT > 5$. The third and higher degree rational approximations are found to be more accurate than any other previous approximation.

Recently Zsakó [1] proposed an empirical formula as an approximation to the integral of the Arrhenius function which is important in the kinetic analysis of thermogravimetric data [2, 3]. Although this integral can be expressed in terms of known functions (an exponential and the exponential integral $E_1(x)$), it is convenient in many applications to have a simple algebraic approximation. Zsakó showed his empirical approximation to be more accurate than those proposed previously by Gorbachev [4] and Coats and Redfern [5]. It is the purpose of this short communication to derive a system of simple algebraic approximations, namely rational approximations, which are more accurate than any previous approximation.

Rational approximation is a method of approximating a function by a ratio of two algebraic polynomials in which the degree of the rational approximation is defined as the degree of the highest degree polynomial. Most often, rational approximations are derived from the power series expansion of the function, such as the methods given by Luke [6].

The integral of the Arrhenius function can be expressed in terms of a dimensionless function, i. e.,

$$\int_0^T \exp(-E/RT)\mathrm{d}T = (E/R)f(x) \tag{1}$$

in which x is E/RT, E is the activation energy and T the temperature. This function $f(x)$ is expressible in terms of known functions, i. e.,

$$f(x) = [\exp(-x)/x] - E_1(x) \tag{2}$$

in which $E_1(x)$ is the exponential integral [7].

Previous algebraic approximation to $f(x)$ have been given by Zsakó [1]

$$f_Z(x) = \exp(-x)/(x - d)(x + 2)$$
$$d = 16/(x_2 - 4x + 84) \quad (3)$$

by Coats and Redfern [5]

$$f_{CR}(x) = (1 - 2/x) \exp(-x)/x^2 \quad (4)$$

and by Gorbachev [4]

$$f_G(x) = \exp(-x)/x(x + 2) \quad (5)$$

Rational approximations for $f(x)$ can be derived knowing Eq. (2) and thus simply using the exponential integral rational approximation already given by Luke [6]. The rational approximations $f_n(x)$ are given in Table 1. Higher degree approximations may be found by consulting Luke [6].

Table 1

Rational approximations for the integral of the Arrhenius function $\int_0^T \exp[-E/RT]dT = (E/R)f(x), \quad x = E/RT$

Degree	$f_n(x)$
1	$\frac{\exp(-x)}{x} \cdot \frac{1}{(x+2)}$
2	$\frac{\exp(-x)}{x} \cdot \frac{(x+4)}{(x^2+6x+6)}$
3	$\frac{\exp(-x)}{x} \cdot \frac{(x^2+10x+18)}{(x^3+12x^2+36x+24)}$
4	$\frac{\exp(-x)}{x} \cdot \frac{(x^3+18x^2+88x+96)}{(x^4+20x^3+120x^2+240x+120)}$

In comparing the approximation, one first observes that the first degree rational approximation is simply the Gorbachev approximation, i. e.,

$$f_1(x) = f_G(x). \quad (6)$$

The relative accuracy of the Zsakó, Gorbachev, Coats and Redfern, and the three lowest degree rational approximation is given in Table 2. The exact value of the Arrhenius function integral has been calculated with the use of the table in reference 7.

An examination of Table 2 reveals that the Coats–Redfern approximation is the least accurate of the approximations studied and that the Gorbachev approximation (which is equivalent to the first degree rational approximation) is to be

Table 2

Relative errors of the various approximations in per cent

E/RT	Coats–Redfern	Gorbachev	Zsakó	2nd Degree Rational	3rd Degree Rational
5	1014	25.7	21.6	9.67	4.33
1	348	17.4	2.91	4.72	1.58
2	100	9.86	0.157	1.66	0.370
5	18.9	3.40	0.200	0.235	0.0239
10	5.17	1.22	0.115	0.0347	1.58×10^{-3}
20	1.38	0.383	0.185	3.75×10^{-3}	6.34×10^{-5}
40	0.358	0.109	0.0823	3.22×10^{-4}	3.16×10^{-7}
100	0.0589	0.0189	0.0172	9.36×10^{-6}	$<10^{-10}$

preferred when an exceptionally simple approximation is needed. An examination of the Zsakó approximation with the second degree approximation (which are of comparable algebraic degree) shows that the second degree rational approximation is to be preferred when $E/RT < 1$ and $E/RT > 5$. For higher accuracy, but with increasing algebraic difficulty, the higher order rational approximation are recommended. For very small values of E/RT ($E/RT < 1$) it may be more preferable to use the power series expansion of the integral of the Arrhenius function, i. e.,

$$\int_0^T \exp[-E/RT]\mathrm{d}T = (E/R)\left[exp(-x)/x + \gamma + \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{nn!} + \ln x\right] \tag{7}$$

in which $x = E/RT$, γ = Euler-Mascheroni constant (0.5 772156649) and truncate the series at the desired accuracy.

*

We wish to acknowledge Meyer Steinberg for his helpful discussion with respect to this communication.

This work was performed under the auspices of the United States Energy Research and Development Administration under Contract No. E(30—1)—16. By acceptance of this article, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

References

1. J. Zsakó, J. Thermal Anal., 8 (1975) 593.
2. J. Zsakó, J. Phys. Chem., 72 (1968) 2406.
3. R. T. Yang and M. Steinberg, J. Phys. Chem., 80 (1976) 965.
4. V. M. Gorbachev, J. Thermal Anal., 8 (1975) 585.
5. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
6. Y. L. Luke, Mathematical Functions and Their Approximations, Academic Press, Inc., New York, 1975, Chapter 13.
7. Handbook of Mathematical Functions, Edited by M. Abramowitz and I. A. Stegun, Dover Publications, Inc., 1965, Chapter 5.