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ORIGINAL PAPER

Rational approximations of the Arrhenius integral using Jacobi fractions and gaussian quadrature

Jorge M. V. Capela · Marisa V. Capela · Clóvis A. Ribeiro

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Abstract The aim of this work is to find approaches for the Arrhenius integral by using the n-th convergent of the Jacobi fractions. The n-th convergent is a rational function whose numerator and denominator are polynomials which can be easily computed from three-term recurrence relations. It is noticed that such approaches are equivalent to the one established by the Gauss quadrature formula and it can be seen that the coefficients in the quadrature formula can be given as a function of the coefficients in the recurrence relations. An analysis of the relative error percentages in the approximations is also presented.

Keywords Nonisothermal kinetic · Arrhenius integral · Jacobi fractions · Three-term recurrence relations · Quadrature formula

1 Introduction

The rate of a condensed-phase chemical reaction has been conveniently parameterized as a function of the temperature τ, and the conversion fraction of the reactant, ϕ as follow:

$$\frac{d\varphi}{dt} = \kappa(\tau) f(\varphi) \tag{1}$$

where $d\varphi/dt$ is the rate of the reaction in a certain instant t and $f(\varphi)$ is the reaction model which describes the dependence of the reaction rate on the extent of the reaction and $\kappa(\tau)$ is a temperature-dependent rate constant. It is usual to suppose $\kappa(\tau)$as the

J. M. V. Capela (✉) · M. V. Capela · C. A. Ribeiro
Instituto de Química, Universidade Estadual Paulista, C.P. 355, Araraquara, SP 14801-970, Brazil
e-mail: capela@iq.unesp.br

Arrhenius equation:

$$\kappa(\tau) = A\,\exp\left(-\frac{E}{R\tau}\right),$$

where A is the Arrhenius pre-exponential factor, E is the activation energy and R is the gas constant [1,2].

The integration of the Arrhenius equation is usually required to perform the kinetic analysis of experimental data obtained under nonisothermal conditions; thus, if the temperature is time-changeable, then the conversional fraction is also temperature dependent. Supposing that temperature variation is conducted at a constant rate, $\beta = d\tau/dt$, Eq. (1) becomes:

$$\frac{d\varphi}{d\tau} = \frac{A}{\beta}\exp\left(-\frac{E}{R\tau}\right) f(\varphi).$$

Rearranging and integrating the above equation for temperature τ varying from 0 to T and the fraction of conversion φ varying from 0 to α, the following equation can be derived:

$$\int_0^{\alpha} \frac{1}{f(\varphi)}d\varphi = \frac{AE}{\beta R} I(x) \tag{2}$$

where $x = E/RT$ and the function $I(x)$ has been defined by the following integral:

$$I(x) = \int_x^{\infty} \frac{\exp(-z)}{z^2} dz. \tag{3}$$

Integration by parts transforms the above integral as follows:

$$I(x) = \frac{\exp(-x)}{x} - \int_x^{\infty} \frac{\exp(-z)}{z} dz,$$

and changing the variable $z = x - w$, the following expression for $I(x)$ is obtained:

$$I(x) = \frac{\exp(-x)}{x}\left(1 - x\int_{-\infty}^{0} \frac{\exp(w)}{x-w}dw\right). \tag{4}$$

The integral $I(x)$, known as the temperature integral or integral of the Arrhenius equation, does not have an exact analytical solution. Several approximated equations to that integral have been proposed in literature. The most popular approximations are imprecise in evaluating the Arrhenius integral when they are compared with those values calculated by numerical integration. This lack of accuracy can cause problems in the estimation of the kinetic parameters [3,4].

The closed form approximations, which result in a more accurate calculation of the Arrhenius integral are those based on rational approximations [5,6].

In this work, the aim is to present new rational approximations to the Arrhenius integral obtained by three-term relation involving the n-th convergent of a Jacobi fraction. In addition, approximations by the gaussian quadrature formula and their comparison to the one obtained from Jacobi fractions have been determined. The calculus of the relative error percentages to the Arrhenius integral approximation regarding some x values were carried out. The numeric and symbolic calculus presented were obtained by using Maxima software.

2 Convergents of the Jacobi fractions

In order to approach the integral in Eq. (4) was considered a sequence $\{Q_n(z)\}$ of polynomials defined by:

$$Q_n(z) = \sum_{k=0}^{n} \left(\frac{n!}{k!}\right)^2 \frac{z^k}{(n-k)!}, \quad n=0,\ 1,\ 2,\ \ldots. \tag{5}$$

The $Q_n(z)$ polynomials are orthogonal to $(-\infty,0)$ values with respect to the weight function $\exp(z)$, which is:

$$\int_{-\infty}^{0} z^s Q_n(z)\exp(z)dz = \left\{\begin{matrix} (n!)^2 & \text{if} \quad s=n \\ 0 & \text{if} \quad 0 \leq \ s \ \leq n-1 \end{matrix}\right\}. \tag{6}$$

The first sequence of polynomials, $\{Q_n(z)\}$ has been defined and, therefore, a second polynomial sequence, $\{P_n(z)\}$, can now be defined:

$$P_n(z) = \int_{-\infty}^{0} \frac{Q_n(z) - Q_n(w)}{z-w} \exp(w)dw, \quad n = 1, 2, \ldots, \tag{7}$$

where $P_n(z)$ is a polynomial of degree $n-1$. These polynomials are known in continued-fraction theory as associated polynomials [7,8].

It is possible to show that the $Q_n(z)$ polynomials can be generated by the following three-term recurrence relation:

$$Q_{n+1}(z) = (z+\alpha_n)\,Q_n(z) - \beta_n Q_{n-1}(z), \quad n = 1, 2, \ldots, \tag{8}$$

with $Q_0(z) = 1, Q_1(z) \ = \ z+1$ and the coefficients are given as $\alpha_n = 2n+1$ and $\beta_n = n^2$.

From definition (7) and using Eqs. (8) and (6), the following expression can be written:

$$P_{n+1}(z) - (z+\alpha_n)\,P_n(z) + \beta_n P_{n-1}(z) = \int_{-\infty}^{0} Q_n(w)\exp(w)dw = 0,$$
$$n = 2,\ 3,\ \cdots$$

Thus, from the equation above, it can be seen that $\{P_n(z)\}$ is a sequence of polynomials generated by the three-term recurrence relation:

$$P_{n+1}(z) = (z + \alpha_n)\, P_n(z) - \beta_n P_{n-1}(z), \quad n = 2, 3, \ldots, \tag{9}$$

with $P_1(z) = 1$ and $P_2(z) = z + 3$.

Those previous three-term relationships suggest that the quotient $P_n(z)/Q_n(z)$ can be considered the n-th convergent of the continued fraction, also called a Jacobi-type continued fraction [8]. On the other hand, from the definition of $P_n(z)$, the following can be obtained:

$$\frac{P_n(x)}{Q_n(x)} = \frac{1}{Q_n(x)} \int_{-\infty}^{0} \frac{Q_n(x) - Q_n(w)}{x - w} \exp(w) dw, \; x > 0,$$

that is:

$$\int_{-\infty}^{0} \frac{\exp(w)}{x - w} dw = \frac{P_n(x)}{Q_n(x)} + \delta(x), \tag{10}$$

where the function $\delta_n(x)$ is defined by:

$$\delta_n(x) = \frac{1}{Q_n(x)} \int_{-\infty}^{0} \frac{Q_n(z)}{x - z} \exp(z) dz. \tag{11}$$

Now, the partial fraction decomposition of the rational function $P_n(z)/Q_n(z)$ in Eq. (10) is defined as:

$$\frac{P_n(z)}{Q_n(z)} = \sum_{k=1}^{n} \frac{c_{nk}}{z - z_{nk}}, \tag{12}$$

where z_{nk} is the k-th zero of $Q_n(z)$ and the coefficients c_{nk} are given by:

$$c_{nk} = \lim_{z \to z_{nk}} \frac{(z - z_{nk})\, P_n(z)}{Q_n(z)} = \frac{P_n\,(z_{nk})}{Q_n'\,(z_{nk})}. \tag{13}$$

Making use of the previous recurrence relation of the polynomials $P_n(z)$ and $Q_n(z)$, it is easy to show that:

$$Q_{n+1}(z) P_n(z) \;-\; P_{n+1}(z) Q_n(z) = -\,\beta_1 \beta_2 \ldots \beta_{n+1}.$$

In particular, if $z = z_{nk}$ then above equation becomes:

$$P_n(z_{nk}) = \frac{-\beta_1 \beta_2 \ldots \beta_{n+1}}{Q_{n+1}\,(z_{nk})}.$$

Therefore the coefficients c_{nk}, defined in Eq. (13), can be written as:

$$c_{nk} = \frac{-\beta_1 \beta_2 \ldots \beta_{n+1}}{Q_{n+1}(z_{nk})\, Q'_n(z_{nk})}. \tag{14}$$

3 Gauss quadrature formula

Another approximation to the integral in Eq. (4) can be obtained by using a quadrature formula. The Gauss quadrature formula will be considered here, in which the nodes z_{nk} are the zeros of the $Q_n(z)$ polynomial [8]:

$$\int_{-\infty}^{0} \frac{\exp(z)}{x - z} dz \approx \sum_{k=1}^{n} \frac{\gamma_{nk}}{z - z_{nk}}, \tag{15}$$

where $\gamma_{n1}, \gamma_{n2}, \ldots, \gamma_{nn}$ are positive numbers, defined by:

$$\gamma_{nk} = \int_{-\infty}^{0} \frac{Q_n(z)}{(z - z_{nk})\, Q'_n(z_{nk})} \exp(z) dz.$$

From the Christoffel-Darboux identity [8], it follows that:

$$\frac{Q_n(z)}{(z - z_{nk})} = \frac{-\beta_1 \beta_2 \ldots \beta_{n+1}}{Q_{n+1}(z_{nk})} \sum_{i=0}^{n} \frac{Q_i(z) Q_i(z_{nk})}{\beta_1 \beta_2 \ldots \beta_{i+1}}$$

and thus the coefficients, γ_{nk}, in the quadrature formula can be written as:

$$\gamma_{nk} = \frac{-\beta_1 \beta_2 \ldots \beta_{n+1}}{Q'_n(z_{nk})\, Q_{n+1}(z_{nk})} \sum_{i=0}^{\infty} \frac{Q_i(z_{nk})}{\beta_1 \beta_2 \ldots \beta_{i+1}} \int_{-\infty}^{0} Q_i(z) \exp(z) dz.$$

As a consequence of the orthogonality property in Eq. (6) and remembering that $Q_0(z) = \beta_1 = 1$, the above equation is simplified as:

$$\gamma_{nk} = \frac{-\beta_1 \beta_2 \ldots \beta_{n+1}}{Q'_n(z_{nk})\, Q_{n+1}(z_{nk})}. \tag{16}$$

Therefore, from Eqs. (14) and (16), it can be seen that:

$$c_{nk} = \gamma_{nk}.$$

By this means, it can also be seen that the breaking down the equation into partial fractions of the rational function $P_n(z)/Q_n(z)$, given in Eq. (12) is equivalent to the quadrature formula in Eq. (15), which is:

$$\frac{P_n(z)}{Q_n(z)} = \sum_{k=1}^{n} \frac{\gamma_{nk}}{z - z_{nk}}. \tag{17}$$

4 Approximations to the Arrhenius integral

Inserting the expression of the right-hand side of Eq. (10) into Eq. (4), it can be seen that the Arrhenius integral is now given by:

$$I(x) = \frac{\exp(-x)}{x}\left(1 - x\frac{P_n(x)}{Q_n(x)}\right) + \exp(-x)\,\delta_n(x), \tag{18}$$

where $P_n(x)/Q_n(x)$ can be determined by recurrence relations (8) and (9), or even by the quadrature formula given in Eq. (17). The term $\delta_n(x)$ is defined in Eq. (11).

The above results suggest the following approximation for the Arrhenius integral:

$$I(x) \;\approx\; I_n(x) = \frac{\exp(-x)}{x}\left(1 - x\frac{P_n(x)}{Q_n(x)}\right), \tag{19}$$

where the error of those approximations can be given by $\exp(-x)\,\delta_n(x)$. Examples of those approximations are presented in Table 1.

The relative error percentages, $\varepsilon_n(x)$, of the Arrhenius integral calculated by means of approximations $I_n(x)$ is defined by the following equation:

$$\varepsilon_n(x) = \frac{\exp(-x)\,\delta_n(x)}{I_n(x) + \exp(-x)\,\delta_n(x)} \times 100\% . \tag{20}$$

In the Table 2, some values of the relative error percentages $\varepsilon_n(x)$ for $n = 1$, 2, 3 and 4 are presented. It can be verified from Table 2 that there is a significant decrease in the $\varepsilon_n(x)$ values with an increase in x, and so on as you progress across the columns of the Table. Moreover, it is worth observing that the errors also decrease with the increasing of the n values in the approximation.

Table 1 Examples of approximations $I_n(x)$

n	$I_n(x)$
1	$\frac{\exp(-x)}{x}\frac{1}{x+1}$
2	$\frac{\exp(-x)}{x}\frac{x+2}{x^2+4x+2}$
3	$\frac{\exp(-x)}{x}\frac{x^2+7x+6}{x^3+9x^2+18x+6}$
4	$\frac{\exp(-x)}{x}\frac{x^3+14x^2+46x+24}{x^4+16x^3+72x^2+96x+24}$

Table 2 Relative error percentages, $\varepsilon_n(x)$, for the approximations of Arrhenius integral $I(x)$ as a function of x for $n = 1$, 2, 3 and 4

x	$\varepsilon_1(x)$	$\varepsilon_2(x)$	$\varepsilon_3(x)$	$\varepsilon_4(x)$
0.1	10.8	7.7	5.7	4.4
0.5	16.1	7.8	3.9	2
1	16.2	5.5	1.9	0.7
1.5	15.3	3.9	1	0.3
2	14.4	2.8	0.6	0.2
2.5	13.5	2.1	0.4	0.1
5	10.1	0.7	0.1	7.5×10^{-3}
10	6.7	0.2	6.3×10^{-3}	3.5×10^{-4}
15	5	0.1	1.4×10^{-3}	4.4×10^{-5}
20	4	3×10^{-2}	3.9×10^{-4}	9×10^{-5}
25	3.3	2×10^{-2}	1.6×10^{-4}	2.5×10^{-6}
30	2.9	1×10^{-2}	7.5×10^{-5}	8.5×10^{-7}
35	2.5	7×10^{-3}	3.8×10^{-5}	3.3×10^{-7}
40	2.2	4.8×10^{-3}	2.1×10^{-5}	1.5×10^{-7}
50	1.8	2.6×10^{-3}	7.5×10^{-6}	3.6×10^{-8}

5 Conclusions

In this article, approximations for the Arrhenius integral based on convergents of the Jacobi fractions are presented. These approximations are easily determined because they are rational functions whose denominator and numerator are polynomials which can be easily generated from three-term recurrence relations. It can still be observed that approximations obtained by Jacobi fractions are equivalent to those established by Gaussian quadrature. The results show that the accuracy of the calculation of the Arrhenius integral depends on values where $x = E/RT$, where E is the activation energy, R is the gas constant and T is the temperature. It can be seen that the error increase when x approaches zero and decreases with the increase in the x values. Increasing the order, (n), of the approximation also decreases the error.

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References

1. L.A. Pérez-Maqueda, P.E. Sánchez-Jiménez, J.M. Criado, Int. J. Chem. Kinet. **37**, 658–666 (2005)
2. S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comput. Sci. **36**, 42–45 (1996)
3. M.E. Brown, *Introduction to Thermal Analysis—Techniques and Applications* (Chapman & Hall, London, 1995)
4. A.K. Galwey, M.E. Brown, *Thermal Decomposition of Ionics Solids, Studies in Physical and Theoretical Chemistry* (Elsevier, 1999)
5. J.H. Flynn, Thermochim. Acta. **300**, 83–92 (1997)
6. L.A. Pérez-Maqueda, J.M. Criado, J. Therm. Anal. Calorim. **60**, 909–915 (2000)
7. A. Erdelyi, *Higher Transcendental Functions*, vol. 2 (McGraw Hill, New York, 1953)
8. T.S. Chihara, *An Introduction to Orthogonal Polynomials, Mathematics and its Applications Series* (Gordon and Breach, 1978)