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THE ACCURACY OF SENUM AND YANG'S APPROXIMATIONS TO THE ARRHENIUS INTEGRAL

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Abstract

The accuracy of the integral of the Arrhenius equation, as determined from the 1st to the 4th degree rational approximation proposed by Senum and Yang, has been calculated. The precision of the 5th to 8th rational approximations, here proposed for the first time, has also been analyzed. It has been concluded that the accuracy increases by increasing the order of the rational approximation. It has been shown that these approximations to the Arrhenius equation integral would allow an accuracy better than 10^{-8}% in the *E/RT* range generally observed for solid state reactions. Moreover, it has been demonstrated that errors closed to 10^{-2}% can be obtained even for $E/RT=1$, provided that high enough degrees of rational approximation have been used. Thus, it would be reasonable to assume that high degree rational approximations for the Arrhenius integral could be used for the kinetic analysis of processes, like adsorption or desorption of gases on solid surfaces, which can take place at low temperatures with very low values of *E/RT*.

Keywords: Arrhenius integral, Senum and Young's approximation

Introduction

The integration of the Arrhenius equation is usually required either for performing the kinetic analysis of experimental data obtained under non-isothermal conditions, or for simulating α–, or $d\alpha/dt$–T plots. A number of different approaches have been proposed in the literature during the second half of the 20th century as can be found in excellent reviews of Šesták [1] and Flynn [2]. It is worth pointing out that the approximations proposed by Senum and Yang [3] have become very popular since they were proposed in 1977, because of their assumed high accuracy. Nowadays, they are still used in a large number of papers [4–16]. These authors have approximated the integral of the Arrhenius equation using rational approximations from 1st to 4th degrees. It is necessary to point out that some expressions similar to those outlined by Senum and Yang were formerly developed by other authors. Thus, the empirical approximation to the Arrhenius integral proposed by Gorbachev [17] is identical to the first rational approximation of Senum and Yang. Zsakó [18] and Balarin [19] also proposed empirical Arrhenius integral equations similar to those developed from the rational approximation. Senum and Yang concluded that higher accuracy is achieved by using the higher order rational approximations.

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However, Urbanovici *et al*. in a very recent paper have calculated [20], the accuracy of these expressions. They have concluded that the precision of the second- and third-order rational approaches is better than that of the fourth-order approximation. This conclusion is in disagreement with both Senum and Yang's statement [3] and the results recently reported by Flynn [2]. Taking into account the generalized use of the Senum and Yang equations for the Arrhenius integral, it seems to be of great interest to check the accuracy of these approximations. The scope of this paper is to re analyze the accuracy of the 2nd to 4th rational approximations proposed by Senum and Yang. Moreover, the precision of the 5th to 8th rational approximations, here proposed for the first time, has been calculated as well.

Results

The general equation describing the rate of a solid state reaction, recorded under a constant heating rate $\beta=\mathrm{d}T/\mathrm{d}t$, can be expressed in the form:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is the reacted fraction at the absolute temperature T; A is the Arrhenius pre-exponential factor, E is the activation energy and $f(\alpha)$ a function depending on the kinetic model obeyed by the reaction.

Equation (1), after being integrated for a linear heating rate experiment with a constant heating rate of β, becomes:

$$g(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \quad (2)$$

The integral of the right hand side of Eq. (2), named the Arrhenius integral, can be expressed in the form:

$$\int_0^T\exp\left(-\frac{E}{RT}\right)\mathrm{d}T=\frac{E}{R}\int_\infty^x\frac{\exp(-x)}{x^2}\mathrm{d}x=\frac{E}{R}p(x) \quad (3)$$

where $x=E/RT$.

The $p(x)$ function cannot be expressed in a closed form and must be calculated by using different approximations [1, 2]. The rational approach proposed by Senum and Yang [3] advocates the use of a certain number of terms in the following continued fraction approximation, previously proposed by Patterson [21, 22]:

$$p(x)=\frac{\exp(-x)}{x}\left(\frac{1}{(x+2)}-\frac{2}{(x+4)}-\frac{6}{(x+6)}-\cdots-\frac{n(n+1)}{(x+2(n+1))}\right)=\frac{\exp(-x)}{x}\pi(x) \quad (4)$$

Urbanovici *et al.* have estimated [20] the accuracy of the 2nd to 4th degree rational approximation described by Senum and Yang [3] and they concluded that, for a particular value of x, the accuracy reaches a maximum for the third-order rational ap-

Table 1 Expressions for one to eight degree rational approximations for Arrhenius integral. The 2nd and 4th degree approximations were proposed by Senum and Yang [3]

Degree	$p(x)$	Equation
1[a]	$\frac{\exp(-x)}{x}\cdot\frac{1}{x+2}$	(5)
2	$\frac{\exp(-x)}{x}\cdot\frac{x+4}{x^2+6x+6}$	(6)
3	$\frac{\exp(-x)}{x}\cdot\frac{x^2+10x+18}{x^3+12x^2+368x+24}$	(7)
4[b]	$\frac{\exp(-x)}{x}\cdot\frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120}$	(8)
5	$\frac{\exp(-x)}{x}\cdot\frac{x^4+28x^3+246x^2+756x+600}{x^5+30x^4+300x^3+1200x^2+1800x+720}$	(9)
6	$\frac{\exp(-x)}{x}\cdot\frac{x^5+40x^4+552x^3+3168x^2+7092x+4320}{x^6+42x^5+630x^4+4200x^3+12600x^2+15120x+5040}$	(10)
7	$\frac{\exp(-x)}{x}\cdot\frac{x^6+54x^5+1070x^4+9720x^3+41112x^2+71856x+35280}{x^7+56x^6+1176x^5+11760x^4+58800x^3+141120x^2+141120x+40320}$	(11)
8	$\frac{\exp(-x)}{x}\cdot\frac{x^7+70x^6+1886x^5+24920x^4+170136x^3+577584x^2+844560x+357120}{x^8+72x^7+2024x^6+28560x^5+216720x^4+880320x^3+1794240x^2+1572480x+403200}$	(12)

[a] This expression was proposed by Gorbachev [17]

[b] Reference [3] has an error in the first power x term of the numerator of the 4th degree approximation, as previously reported by Flynn [2]. It should be written $86x$ instead of $88x$

Table 2 Percentage errors of the $p(x)$ functions for the 2nd to 8th rational approximations

x	Degree							
	1	2	3	4	5	6	7	8
1	-17.421	-4.716	-1.584	$-6.082\cdot10^{-1}$	$-2.567\cdot10^{-1}$	$-1.163\cdot10^{-1}$	$-5.568\cdot10^{-2}$	$-3.334\cdot10^{-2}$
2	-9.859	-1.664	$-3.703\cdot10^{-1}$	$-9.833\cdot10^{-2}$	$-2.961\cdot10^{-2}$	$-9.813\cdot10^{-3}$	$-3.508\cdot10^{-3}$	$-1.732\cdot10^{-3}$
5	-3.403	$-2.354\cdot10^{-1}$	$-2.393\cdot10^{-2}$	$-3.132\cdot10^{-3}$	$-4.927\cdot10^{-4}$	$-8.924\cdot10^{-5}$	$-1.810\cdot10^{-5}$	$-6.369\cdot10^{-6}$
10	-1.225	$-3.474\cdot10^{-2}$	$-1.583\cdot10^{-3}$	$-9.931\cdot10^{-5}$	$-7.886\cdot10^{-6}$	$-7.524\cdot10^{-7}$	$-8.325\cdot10^{-8}$	$-2.178\cdot10^{-8}$
20	$-3.825\cdot10^{-1}$	$-3.756\cdot10^{-3}$	$-6.409\cdot10^{-5}$	$-1.604\cdot10^{-6}$	$-5.354\cdot10^{-8}$	$-2.244\cdot10^{-9}$	$-1.137\cdot10^{-10}$	$-2.294\cdot10^{-11}$
30	$-1.847\cdot10^{-1}$	$-9.154\cdot10^{-4}$	$-8.179\cdot10^{-6}$	$-1.106\cdot10^{-7}$	$-2.050\cdot10^{-9}$	$-4.916\cdot10^{-11}$	$-1.768\cdot10^{-12}$	$-5.745\cdot10^{-13}$
40	$-1.085\cdot10^{-1}$	$-3.239\cdot10^{-4}$	$-1.781\cdot10^{-6}$	$-1.510\cdot10^{-8}$	$-1.789\cdot10^{-10}$	$-3.226\cdot10^{-12}$	$-5.376\cdot10^{-13}$	$<10^{-13}$
50	$-7.137\cdot10^{-2}$	$-1.422\cdot10^{-4}$	$-5.296\cdot10^{-7}$	$-3.080\cdot10^{-9}$	$-2.579\cdot10^{-11}$	$-7.941\cdot10^{-13}$	$<10^{-13}$	
75	$-3.291\cdot10^{-2}$	$-3.092\cdot10^{-5}$	$-5.540\cdot10^{-8}$	$-1.585\cdot10^{-10}$	$-7.353\cdot10^{-13}$	$<10^{-13}$		
100	$-1.886\cdot10^{-2}$	$-1.028\cdot10^{-5}$	$-1.080\cdot10^{-8}$	$-1.847\cdot10^{-11}$	$<10^{-13}$			

proximation. Thus, they consider that the use of approximations with order higher than three is not justified. However, Flynn [2] has pointed out that there is an error in the first power of the x term of the numerator of the 4th degree rational approximation proposed by Senum and Yang. According to Flynn, the correct value of this term is 86x, instead of 88x as reported by Senum and Yang [3]. The equation used by Urbanovici *et al.* [20] for determining the accuracy of the fourth-order approximation was that proposed by Senum and Yang.

The expressions for the $p(x)$ function calculated by developing Eq. (4) by means of the symbolic calculation pad included in the MathCad software [23], after considering from the second to the eighth degree rational approximation, are shown in Table 1. Equation (7) obtained for the 4th rational approximation is identical to the one reported by Flynn [2]. Thus, the results reported here corroborate Flynn's finding concerning the error in the coefficient of the first power of the x term of the numerator of the 4th degree approximation given by Senum and Yang [3]. Therefore, the accuracy values that Urbanovici *et al.* have calculated for this approximation, using the equation previously reported by Senum and Yang, could be wrong.

The Arrhenius integral has been determined as a function of the x parameter by numerical integration with the highest precision (10^{-13}%) allowed by MathCad software [23] used. The values obtained have been compared with those calculated from Eqs (5) to (12), included in Table 1, and the corresponding relative errors have been included in Table 2.

Table 3 Expressions for different rational approximations for Arrhenius integral proposed in the literature

Author	$p(x)$	Equation
Doyle [24], Coats–Redfern [25]	$\frac{\exp(-x)}{x}\cdot\frac{1}{x}$	(13)
Coats–Redfern [25]	$\frac{\exp(-x)}{x}\cdot\frac{x-2}{x}$	(14)
Balarin [19]	$\frac{\exp(-x)}{x}\cdot\frac{x^3-2x^2+6x-20}{x^4}$	(15)
Zsakó [18]	$\frac{\exp(-x)}{x}\cdot\frac{x^3+4x^2+84x}{x^4+2x^3+76x^2+152x-32}$	(16)

For the sake of completeness it has been considered of interest to analyze the accuracy of the $p(x)$ functions whose $\pi(x)$ expressions (Eq. 4) are given by a ratio of two algebraic polynomials like the rational approximations. These functions, as reviewed by Šesták [1], are summarized in Table 3. The percentage errors, percentage calculated following the same procedure previously described for determining the relative error of Eqs (5) to (12) are shown in Table 4. The results obtained are in good agreement with those previously determined by Šesták [1] in the range $5\leq x\leq 40$. The accuracy of these Arrhenius integral approximations is poorer than the corresponding ones for the rational approach with an order higher than two as a comparison of the results included in Tables 2 and 4 shows.

Table 4 Percentage error of the $p(x)$ included in Table 3

x	Approximation			
	Doyle [24] and Coats–Redfern [25]	Coats–Redfern [25]	Balarin [19]	Zsakó [18]
1	147.737	–347.737	–3816.066	2.906
2	80.282	–100	–280.282	$1.568\cdot10^{-1}$
5	35.236	–18.86	–8.039	$2.002\cdot10^{-1}$
10	18.530	–5.176	$-4.346\cdot10^{-1}$	$-1.150\cdot10^{-1}$
20	9.579	–1.379	$-8.964\cdot10^{-3}$	$-1.849\cdot10^{-1}$
30	6.470	$-6.284\cdot10^{-1}$	$2.570\cdot10^{-3}$	$-1.231\cdot10^{-1}$
40	4.886	$-3.583\cdot10^{-1}$	$2.268\cdot10^{-3}$	$-8.232\cdot10^{-2}$
50	3.926	$-2.313\cdot10^{-1}$	$1.541\cdot10^{-3}$	$-5.795\cdot10^{-2}$
75	2.633	$-1.040\cdot10^{-1}$	$6.124\cdot10^{-4}$	$-2.897\cdot10^{-2}$
100	1.981	$-5.886\cdot10^{-2}$	$2.924\cdot10^{-4}$	$-1.721\cdot10^{-2}$

Conclusions

The above results point out that the accuracy of the integration of the Arrhenius equation increases by increasing the degree of the rational approximation. These results are in agreement with Senum and Yang's [3] statement and Flynn's previous calculations [2], while they are in disagreement with the conclusion of Urbanovici *et al.* [20]. On the other hand, it must be pointed out that, in spite of the fact that values of $x=E/RT<10$ are generally meaningless in solid state reactions we have extended the calculations down to $x=1$. The results obtained demonstrate that errors close to $10^{-2}\%$ can be reached for values of $x=1$ provided that high enough rational approximation degrees have been used. This finding suggests that the use of high-degree rational approximations for determining the $p(x)$ function would be useful for performing the kinetic analysis of adsorption and desorption of gases on solid surfaces. These processes frequently take place below room temperature and very low values of E/RT are not unusual. However, the choice of the proper approximation for the Arrhenius integral depends on the value of E/RT and the desired accuracy, which must be consistent with the experimental error, rather than on the specific type of reaction.

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