Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 325-327

ON THE ACCURACY OF SENUM AND YANG'S FOURTH DEGREE RATIONAL APPROXIMATION OF THE TEMPERATURE INTEGRAL

E. Urbanovici[1], *C. Popescu*[1] *and E. Segal*[2*]

[1]LACECA Research Center, Str. Siret nr. 95, 78308 Bucharest
[2]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest
Bd. Republicii 13, Bucharest, Romania

In non-isothermal kinetics, for the most usual case of a linear heating programme corresponding to a constant heating rate (β), the dependence of the degree of conversion (α) on temperature (T) is described by the well-known integral rate equation [1, 2]

$$g(\alpha) = (A/\beta)\int_0^T \exp[-E/RT]\mathrm{d}T \tag{1}$$

where A is the preexponential factor, E is the activation energy while $g(\alpha)$ is a function depending on the mechanism of reaction.

The integral from the right-hand side of Eq. (1) is frequently met in non-isothermal kinetics and is called the temperature integral. It has no exact analytical solution, but it can be approximated as follows [3, 4]:

$$\int_0^T \exp[-E/RT]\mathrm{d}T = (E/R)(1/x^2)\exp[-x]Q(x) \tag{2}$$

where $x=E/RT$ and $Q(x)$ is a function which changes slowly with x and is close to unity.

In the literature one can find several particular forms of $Q(x)$ [4, 5], but in the following treatment we are going to pay attention to the second, third and fourth degree rational approximations proposed by Senum and Yang [6]. For these particular cases $Q(x)$ can be expressed as

$$Q_2(x) = (x^2 + 4x) / (x^2 + 6x + 6) \tag{3}$$

* Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$$Q_3(x) = (x^3 + 10x^2 + 18x) / (x^3 + 12x^2 + 36x + 24) \quad (4)$$

and

$$Q_4(x) = (x^4 + 18x^3 + 88x^2 + 96x) / (x^4 + 20x^3 + 120x^2 + 240x + 120) \quad (5)$$

where the indices of $Q(x)$ refer to the order of approximation.

Although Senum and Yang presented in their paper no data about the accuracy of the fourth degree rational approximation, it has been assumed as having a better accuracy than the lower degree rational approximations, and was thus widely used in the last two decades [7–16]. This is due probably to the following assumption made by Senum and Yang: 'For higher accuracy, but with increasing algebraic difficulty, the higher order rational approximations are recommended' [6].

As far as we are concerned, it was in 1990 that for the first time some results concerning the accuracy of the Senum and Yang's fourth degree rational approximation were presented [4]. It was shown that for usual values of x this approximation leads to even less accurate evaluation of the temperature integral than Senum and Yang's second and third degree rational approximations, i.e. for $5<x<100$ the relative error of this approximation is lying between 0.905% and $1.683 \cdot 10^{-2}$%. On the other hand, in a relatively recent paper Málek *et al.* [14] have pointed out that according to their experiences it is sufficiently precise to use Senum and Yang's fourth degree rational approximation which gives errors lower than 10^{-5}% for $x>20$. A similar statement was made by Criado *et al.* in [12].

In order to clarify these conflicting results we have evaluated numerically the temperature integral for a number of usual values of x lying between 5 and 200. The numerical calculations were performed with a precision higher than $\pm 10^{-11}$% by using the 'NIntegrate' function of the Mathematica software system [17, 18]. The values obtained in this way have been compared with those evaluated by

Table 1 Relative errors of Senum and Yang's 2nd, 3rd and 4th degree rational approximations in per cent

x	$Q_2(x)$	$Q_3(x)$	$Q_4(x)$
5	$-2.354 \cdot 10^{-1}$	$-2.393 \cdot 10^{-2}$	$9.051 \cdot 10^{-1}$
10	$-3.474 \cdot 10^{-2}$	$-1.583 \cdot 10^{-3}$	$5.324 \cdot 10^{-1}$
20	$-3.756 \cdot 10^{-3}$	$-6.409 \cdot 10^{-5}$	$2.351 \cdot 10^{-1}$
30	$-9.154 \cdot 10^{-4}$	$-8.179 \cdot 10^{-6}$	$1.308 \cdot 10^{-1}$
40	$-3.239 \cdot 10^{-4}$	$-1.781 \cdot 10^{-6}$	$8.304 \cdot 10^{-2}$
50	$-1.422 \cdot 10^{-4}$	$-5.296 \cdot 10^{-7}$	$5.734 \cdot 10^{-2}$
75	$-3.092 \cdot 10^{-5}$	$-5.540 \cdot 10^{-8}$	$2.832 \cdot 10^{-2}$
100	$-1.028 \cdot 10^{-5}$	$-1.080 \cdot 10^{-8}$	$1.683 \cdot 10^{-2}$
150	$-2.136 \cdot 10^{-6}$	$-1.040 \cdot 10^{-9}$	$7.909 \cdot 10^{-3}$
200	$-6.933 \cdot 10^{-7}$	$-1.935 \cdot 10^{-10}$	$4.578 \cdot 10^{-3}$

Senum and Yang's second, third and fourth degree rational approximations by determining the corresponding relative errors. Table 1 shows the obtained results.

The data presented in Table 1 confirm our previous results, namely that the accuracy of both the second and third degree rational approximations is better than that of the fourth degree rational approximation. We consider, therefore, that in the following the use of Senum and Yang's fourth degree rational approximation of the temperature integral is not justified.

* * *

One of the authors (E. U.) is indebted to the Alexander von Humboldt Foundation (Germany) for the financial support provided for his scientific activity.

References

1 J. H. Flynn and L. A. Wall, J. Res. Natl. Bur. Stand., Sect. A, 70 (1966) 487.
2 J. Šesták, V. Šatava and W. W. Wendlandt, Thermochim. Acta, 7 (1973) 447.
3 G. Várhegyi, Thermochim. Acta, 25 (1978) 201.
4 E. Urbanovici and E. Segal, Thermochim. Acta, 168 (1990) 71.
5 J. Zsakó, J. Thermal Anal., 34 (1988) 1489.
6 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1977) 445.
7 J. M. Criado and A. Ortega, Thermochim. Acta, 44 (1981) 239.
8 L. Reich and S. S. Stivala, Thermochim. Acta, 52 (1982) 337.
9 L. Reich and S. S. Stivala, Thermochim. Acta, 55 (1982) 385.
10 S. V. Vyazovkin, I. S. Romanovsky and A. I. Lesnikovich, J. Thermal Anal., 34 (1988) 239.
11 S. V. Vyazovkin, A. I. Lesnikovich and I. S. Romanovsky, J. Thermal Anal., 34 (1988) 609.
12 J. M. Criado, M. González, A. Ortega and C. Real, J. Thermal Anal., 34 (1988) 1387.
13 E. Urbanovici and E. Segal, Thermochim. Acta, 141 (1989) 9.
14 J. Málek, J. Šesták, F. Rouquerol, J. Rouquerol, J. M. Criado and A. Ortega, J. Thermal Anal., 38 (1992) 71.
15 J. Málek, Thermochim. Acta, 222 (1993) 105.
16 J. Málek and J. M. Criado, Thermochim. Acta, 236 (1994) 187.
17 S. Wolfram, Mathematica®-A system for Doing Mathematics by Computer, Addison-Wesley, Reading, Massachusetts, 1991, 686.
18 T. B. Bahder, Mathematica® for Scientist and Engineers, Addison-Wesley, Reading, Massachusetts, 1995, 381.