Approximations for the generalized temperature integral: a method based on quadrature rules

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Abstract The generalized temperature integral $I(m, x)$ appears in non-isothermal kinetic analysis when the frequency factor depends on the temperature. A procedure based on Gaussian quadrature to obtain analytical approximations for the integral $I(m, x)$ was proposed. The results showed good agreement between the obtained approximation values and those obtained by numerical integration. Unless other approximations found in literature, the methodology presented in this paper can be easily generalized in order to obtain approximations with the maximum of accurate.

Keywords Non-isothermal kinetics · Generalized temperature integral · Gaussian quadrature

Introduction

Generally, it is assumed that the kinetic equation of a condensed-phase chemical reaction depends on the temperature, τ, and conversion fraction of the reactant, ϕ, and is represented by:

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

where $d\varphi/dt$ is the rate of the reaction at 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

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constant. It is usual to suppose $\kappa(\tau)$ as being the Arrhenius expression

$$\kappa(\tau) = A\exp\left(-\frac{E}{R\tau}\right) \tag{2}$$

where A is the Arrhenius pre-exponential factor, E is the activation energy and R is the gas constant [1, 2]. The pre-exponential factor can be associated with temperature by the following relationship

$$A = A_0\tau^m, \tag{3}$$

where A_0 is a constant and values of the exponent m range from -1.5 to 2.5 for some solid-state reactions [3].

The integral form of the reaction model is defined by

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\varphi)}d\varphi \tag{4}$$

where α is the reacted fraction at time t. Some important reaction models used in kinetic analysis of solid-state reactions can be found in literature [1, 2, 4, 5].

Under non-isothermal conditions of a linear temperature program, the conversional fraction is also temperature dependent. If Eq. 3 is fulfilled and temperature variation is conducted at a constant rate, $\beta = d\tau/dt$, then the kinetic equation is given by

$$\frac{d\varphi}{d\tau} = \frac{A_0\tau^m}{\beta}\exp\left(-\frac{E}{R\tau}\right)f(\varphi). \tag{5}$$

If α and T are the reacted fraction and the temperature at the time t, respectively, then the integration of Eq. 5 for $0 \leq \varphi \leq \alpha$ and $0 \leq \tau \leq T$ leads to

$$g(\alpha) = \frac{A_0}{\beta}\int_0^T \tau^m\exp\left(-\frac{E}{R\tau}\right)d\tau \tag{6}$$

where $g(\alpha)$ is the function defined in Eq. 4. The change of variable $z = E/R\tau$ transforms the above equation into

$$g(\alpha) = \frac{A_0}{\beta}\left(\frac{E}{R}\right)^{m+1} \int_x^\infty \frac{\exp(-z)}{z^{m+2}}\,dz \qquad (7)$$

where $x = E/RT$.

The integral of the right side of Eq. 7, known as the generalized temperature integral, does not have an exact analytical solution and should be used a method of approximation [6, 7]. Although the numerical integration provides excellent results for the integral value, the aim of the kinetic analysis is to determine the E and A_0 parameters from Eq. 7 and not only the accurate numerical evaluation of the integral. Thus, it is necessary to use an analytical approximation in place of the numerical integration to obtain estimates for the parameters E and A_0.

In literature, analytical approximations that can be used for evaluation of the generalized temperature integral are found. Techniques for the development of the integral calculation were created by Singh et al. [8] and Gartia et al. [9] but they are complex and demand long computing time. In a different way, Wanjun et al. [10] presented two approximations for temperature integral which are simple to use, accurate and valid for arbitrary m values. Cai and Liu [6, 7] also proposed a simple integral approximation easy to be used and more accurate than the Wanjun one.

However, the methods employed by the above authors are not easily generalized in order to obtain formulas with the maximum accuracy. As this problem can be solved by using quadrature rules, the aim of this work is to present analytical approximations for the general temperature integral based on Gaussian quadrature. It will be shown, for some values of m, the results calculated by that approximations are in agreement with those one obtained by numerical integration. In addition, a comparison will be made with the results obtained by Cai and Liu [6, 7].

Theory

Considering:

$$I(m,x) = \int_x^\infty \frac{\exp(-z)}{z^{m+2}}\,dz \qquad (8)$$

as the generalized temperature integral in Eq. 7 and substituting $z = x - w$, the integral $I(m, x)$ can be changes as follow:

$$I(m,x) = \exp(-x) \int_{-\infty}^0 \frac{\exp(w)}{(x-w)^{m+2}}\,dw. \qquad (9)$$

According to the Gauss quadrature method [11], the integrals from Eq. 9 can be also written as

$$\int_{-\infty}^0 \frac{\exp(w)}{(x-w)^{m+2}}\,dw \approx \sum_{k=1}^n \frac{\gamma_{nk}}{(x-z_{nk})^{m+2}}, \qquad (10)$$

where z_{nk} is the k-th zero of polynomial $Q_n(z)$ defined by [12]:

$$Q_n(z) = \sum_{k=0}^n \left(\frac{n!}{k!}\right)^2 \frac{z^k}{(n-k)!}, \quad n = 0, 1, 2, \ldots \qquad (11)$$

The coefficients γ_{nk} in Eq. 10 are given by [11, 12]:

$$\gamma_{nk} = \frac{-1 \cdot 4 \cdot 9 \ldots n^2}{Q_n'(z_{nk})Q_{n+1}(z_{nk})}. \qquad (12)$$

Thus, from previous equations, the following functions $I_n(m, x)$ can be obtained as approximations of the integral $I(m, x)$:

$$I_n(m,x) = \frac{\exp(-x)}{x^{m+2}} \sum_{k=1}^n \gamma_{nk}\left(\frac{x}{x-z_{nk}}\right)^{m+2}. \qquad (13)$$

Results and discussion

The accuracy for the approximations of $I_2(m, x)$ and $I_3(m, x)$, defined by Eq. 13 will be examined. In case of function $I_2(m, x)$ it is not difficult to show that:

$$I_2(m,x) = \frac{\exp(-x)}{x^{m+2}}\left[\frac{(2-\sqrt{2})}{4}\left(\frac{x}{x+2+\sqrt{2}}\right)^{m+2} + \frac{(2+\sqrt{2})}{4}\left(\frac{x}{x+2-\sqrt{2}}\right)^{m+2}\right]. \qquad (14)$$

For the function $I_3(m, x)$ the values of the γ_{3k} and z_{3k} in Eq. 13 are given in Table 1.

The following approximation, Eq. 15, proposed by Cai and Liu [6, 7], has been considered for comparison:

$$p_{1m}(x) = \frac{\exp(-x)}{x^{m+2}}\frac{0.99954x - 0.044967m + 0.58058}{x + 0.94057m + 2.5400} \qquad (15)$$

The relative error percentage of the proposed approximations from Eq. 13 can be defined by the following equation

$$\varepsilon(m,x) = \left|\frac{I(m,x) - I_n(m,x)}{I(m,x)}\right| \times 100\%, \qquad (16)$$

where $I_n(m, x)$ is the analytical approximation given by Eq. 13 and $I(m, x)$ is obtained by numerical integration. For the Cai and Liu approximation $I_n(m, x)$ is replaced by $p_{1m}(x)$, given in Eq. 15.

Table 1 Values of the γ_{3k} and z_{3k} of the function $I_3(m, x)$

k	z_{3k}	γ_{3k}
1	−0.41577455678348	0.7110930099291700
2	−2.294280360279042	0.2785177335692400
3	−6.289945082937479	0.010389256501586

Table 2 Relative error percentages of the $I_2(m, x)$ approximation

x	m							
	−1.5	−1	0	0.5	1	1.5	2	2.5
5	3.7×10^{-2}	1.2×10^{-1}	5.2×10^{-1}	8.6×10^{-1}	1.3×10^{0}	1.9×10^{0}	2.6×10^{0}	3.5×10^{0}
10	4.4×10^{-3}	1.5×10^{-2}	6.9×10^{-2}	1.2×10^{-1}	1.9×10^{-1}	2.7×10^{-1}	3.9×10^{-1}	5.3×10^{-1}
15	1.1×10^{-3}	4.0×10^{-3}	1.8×10^{-2}	3.2×10^{-2}	5.1×10^{-2}	7.7×10^{-2}	1.1×10^{-1}	1.5×10^{-1}
20	4.2×10^{-4}	1.5×10^{-3}	6.9×10^{-3}	1.2×10^{-2}	1.9×10^{-2}	2.9×10^{-2}	4.3×10^{-2}	5.9×10^{-2}
30	9.6×10^{-5}	3.4×10^{-4}	1.6×10^{-3}	2.9×10^{-3}	4.7×10^{-3}	7.2×10^{-3}	1.0×10^{-2}	1.5×10^{-2}
50	1.4×10^{-5}	5.1×10^{-5}	2.5×10^{-4}	4.4×10^{-4}	7.2×10^{-4}	1.1×10^{-3}	1.6×10^{-3}	2.3×10^{-3}
100	9.8×10^{-7}	3.6×10^{-6}	1.8×10^{-5}	3.1×10^{-5}	5.2×10^{-5}	8.0×10^{-5}	1.2×10^{-4}	1.7×10^{-4}

Table 3 Relative error percentages of the $I_3(m, x)$ approximation

x	m							
	−1.5	−1	0	0.5	1	1.5	2	2.5
5	2.8×10^{-3}	1.1×10^{-2}	6.0×10^{-1}	1.1×10^{-1}	1.8×10^{-1}	2.9×10^{-1}	4.4×10^{-1}	6.2×10^{-1}
10	1.4×10^{-4}	5.8×10^{-4}	3.5×10^{-3}	6.7×10^{-3}	1.2×10^{-2}	1.9×10^{-2}	3.0×10^{-2}	4.5×10^{-2}
15	2.0×10^{-5}	8.5×10^{-5}	5.3×10^{-4}	1.0×10^{-3}	1.9×10^{-3}	3.1×10^{-3}	5.0×10^{-3}	7.6×10^{-3}
20	4.8×10^{-6}	2.0×10^{-5}	1.3×10^{-4}	2.6×10^{-4}	4.7×10^{-4}	7.9×10^{-4}	1.3×10^{-3}	1.9×10^{-3}
30	5.6×10^{-7}	2.4×10^{-6}	1.6×10^{-5}	3.2×10^{-5}	5.9×10^{-5}	1.0×10^{-4}	1.6×10^{-4}	2.6×10^{-4}
50	3.4×10^{-8}	1.5×10^{-7}	9.9×10^{-7}	2.0×10^{-6}	3.8×10^{-6}	6.6×10^{-6}	1.1×10^{-5}	1.7×10^{-5}
100	6.5×10^{-10}	2.9×10^{-9}	2.0×10^{-8}	4.0×10^{-8}	7.6×10^{-8}	1.3×10^{-7}	2.2×10^{-7}	3.6×10^{-7}

Table 4 Relative error percentages of the $p_{1m}(x)$ approximation

x	m							
	−1.5	−1	0	0.5	1	1.5	2	2.5
5	3.7×10^{-2}	3.5×10^{-3}	5.1×10^{-2}	1.1×10^{-1}	1.7×10^{-1}	2.2×10^{-1}	2.6×10^{-1}	2.9×10^{-1}
10	2.8×10^{-2}	1.9×10^{-3}	3.4×10^{-2}	4.7×10^{-2}	6.0×10^{-2}	7.3×10^{-2}	8.9×10^{-2}	1.1×10^{-1}
15	2.0×10^{-2}	3.6×10^{-2}	4.7×10^{-3}	1.4×10^{-2}	2.4×10^{-2}	3.5×10^{-2}	4.8×10^{-2}	6.3×10^{-2}
20	1.2×10^{-2}	1.2×10^{-2}	8.7×10^{-3}	5.3×10^{-3}	5.9×10^{-4}	5.5×10^{-3}	1.3×10^{-2}	2.2×10^{-2}
30	3.1×10^{-4}	5.3×10^{-3}	1.3×10^{-2}	1.6×10^{-2}	1.7×10^{-2}	1.7×10^{-2}	1.6×10^{-2}	1.4×10^{-2}
50	1.5×10^{-2}	7.7×10^{-3}	4.5×10^{-3}	9.6×10^{-3}	1.4×10^{-2}	1.8×10^{-2}	2.1×10^{-2}	2.4×10^{-2}
100	2.9×10^{-2}	2.3×10^{-2}	1.8×10^{-2}	9.2×10^{-3}	4.8×10^{-3}	7.0×10^{-4}	3.2×10^{-3}	6.9×10^{-3}

The relative error percentages of $I_2(m, x)$ and $I_3(m, x)$ are listed in Tables 2 and 3, respectively. The relative error percentages of the Cai and Liu approximation are given in Table 4.

From Tables 2, 3, 4 one can see that the relative errors depend on the values of m and x, that is, depend on temperature and activation energy values. It can be also seen that the error increases when x increases and decreases with the decrease of the one. Increasing the order n of the approximation $I_n(m, x)$ the error is also decreased.

The results presented in the Table 2 show that the $I_2(m, x)$ approximation is not as accurate as Cai and Liu one, Table 4, only for lower x values. Moreover, the $I_3(m, x)$ approximation, Table 3, is equivalent to the $p_{1m}(x)$ one, Table 4, for lower x values and is significantly more accurate for the higher x values.

Conclusions

As the generalized temperature integral $I(m, x)$ does not have a closed-form solution, approximations must be obtained to find appropriate estimates for parameters A_0 and E. Analytical approximations, $I_n(m, x)$, based on

Gaussian quadrature was developed. The results obtained demonstrate that the errors are small, that is, the values of the $I(m, x)$ integral obtained by $I_n(m, x)$ functions are like similar to those obtained by numerical integration. Moreover, the results point out that the accuracy of integration depends on the x values and that the accuracy can be improved choosing an appropriate n value.

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