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THE ACCURACY OF EQUATIONS APPROXIMATING THE TEMPERATURE INTEGRAL

PART I.

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Results of an evaluation of the approximation accuracy of the temperature integral obtained by means of different approximation equations are presented. The usability for approximation purposes of the Schloemilch, asymptotic, Bernoullie and Vallet series, depending on the number of expansion terms used in calculations, and the Doyle logarithmic, Zsakó, Coats—Redfern and Turner—Schnitzer—Gorbachev equations has been evaluated. Boundary values of z, above which the approximation accuracy of a given equation is higher than or equal to the assumed one, are given.

The already widespread measurements of the kinetics of chemical reactions under linear temperature increase conditions have emphasized the need for a knowledge of the value of the integral shown below when elaborating experimental results:

$$J = \int_{T_0}^{T_a} \exp(-E/RT)\,\mathrm{d}T \tag{1}$$

where E is the activation energy, R the gas constant and T, T_0 and T_a are the absolute, initial and final temperatures, respectively.

This integral can be rearranged to a simpler form by introducing

$$x = E/RT \tag{2}$$

Hence

$$J = \frac{E}{R}\int_{z_0}^{z} \frac{\exp(-x)}{x^2}\,\mathrm{d}x \tag{3}$$

where

$$z_0 = E/RT_0 \tag{4}$$

or in another way

$$J = \frac{E}{R}(L(z) - L(z_0)) \tag{5}$$

where

$$L(z) = \int_{z}^{\infty} \frac{\exp(-x)}{x^2}\,\mathrm{d}x \tag{6}$$

Integral $L(z)$ is a convergent integral and cannot be expressed in the form of elementary functions. Thus, for practical purposes, $L(z)$ values [1, 2] taken from tables or calculated from approximative equations [3] are used.

The accuracy of different approximative equations is different and for a given approximative equation it may also be different for different z values. With regard to the method of calculating the value of integral J via Eq. (5), it is important that the approximation errors of both integrals $L(z_0)$ be of the same sign. Since this error has the character of a systematic one, it is constant with regard to its sign within a given variability range.

The aim of the present paper is to evaluate the accuracy of the approximation to the integral $L(z)$ using generally encountered approximative equations. For each approximative equation discussed here, the approximation error has been calculated and its sign is given. Calculations were made for $z \langle 1.70 \rangle$ every 5 units. This range covers most of the values encountered in practice.

In this paper an analysis is made merely of approximative equations which are given in the form of a function of variable z. Other equations, e.g. the MacCallum–Tanner equation [4], where E and T are in the apparent form, will be analyzed separately. The error of the approximative equation is defined by

$$B = \frac{D-A}{D} 100\% \tag{7}$$

where D is the accurate value of integral $L(z)$, and A is the value calculated from the given approximative equation. The value B of the error has been assumed as the basis for determining the limits of applicability of the respective approximative equations. The intermediate values of the error have been calculated by the method of linear interpolation. Hence, the boundary values shown in the tables are higher than the accurate ones.

The numerically calculated values of integral $L(z)$ have been assumed as values D. The calculations of the value D were carried out twice, using the Gauss and Simpson methods [5]. The error of value D was found not to be higher than 1.10^{-8} of the value of $L(z)$. The calculated D values are in agreement with those given by Doyle [1].

The Schloemilch series [6]

The Schloemilch series, often encountered in the literature [3, 7, 8], is given to an accuracy of two, four or eight terms

$$L(z) \approx \frac{\exp(-z)}{z(z+1)} \left\{1 - \frac{1}{(z+2)} + \frac{2}{(z+2)(z+3)} - \frac{4}{(z+2)\dots(z+4)} + \frac{14}{(z+2)\dots(z+5)} - \frac{38}{(z+2)\dots(z+6)} + \frac{216}{(z+2)\dots(z+7)} - \frac{600}{(z+2)\dots(z+8)} + \dots\right\} \tag{8}$$

As a particular case of the Schloemilch series, the Turner–Schnitzer equation [9] may be considered, which has been presented for the second time by Gorbachev [10]. This equation has been obtained from Eq. (8) by limiting this series to the two first terms. In order to evaluate the effect of the expansion of the Schloemilch series on the approximation accuracy, calculations were made limiting this series to two, three or more terms.

The calculations carried out have shown that the Schloemilch series approximates the $L(z)$ integral very well. The accuracy of approximation increases very rapidly with the increase of the number of terms used, as well as with the increase of z. For $z = 70$, the accuracy of the eight-term series is more than $1.10^{-8}\%$. The values of error B are positive when the series has an even number of terms, being negative in the opposite case. For the Schloemilch series limited to five or eight terms, a change in the sign of error B is observed when $z < 5$. Boundary values z are given in Table 1, above which expansion of the Schloemilch series will make it possible to determine value $L(z)$ with an accuracy equal to or higher than the assumed one. The data contained in Table 1 confirm Zsakó's opinion [11] on the accuracy of the Turner–Schnitzer–Gorbachev equation. For $z > 18$ an accuracy of the above mentioned equation higher than 0.5% was obtained. Attention must only be paid to the fact that for less accurate calculations, with an accuracy of about 3%, the Schloemilch series limited to the first term alone is sufficient.

Table 1

Boundary values of z for the Schloemilch series for an assumed approximation error

Number of expansion terms	Approximation error not above %						Sign of error	Remarks
	3	1	0.5	0.1	0.01	0.001		
1	30.5	#	#	#	#	#	–	
2	6.0	10.4	17.7	42.0	#	#	+	Turner–Schnitzer–Gorbachev equation
3	1.3	4.0	5.8	13.0	30.6	69.9	–	
4	2.0	2.9	4.2	8.7	16.0	30.8	+	
5	1.0	1.0	1.0	3.3	9.3	17.5	–	
6	1.0	2.1	2.6	4.1	8.9	13.5	+	
7	1.0	1.0	1.9	3.0	3.7	4.8	–	
8	1.0	1.2	2.2	3.0	4.9	9.5	+	

Asymptotic series

The asymptotic series is used relatively often in the calculations:

$$L(z) = \frac{\exp(-z)}{z^2}\left(1 - \frac{2!}{z} + \frac{3!}{z^2} + \ldots + (-1)^{n+1}\frac{n!}{z^{(n-1)}}\right) \tag{9}$$

According to Flynn and Wall [3], this series may be used for $z > 10$, provided the number of terms used is lower than z. The Doyle [1] and Coats–Redfern equations [12] are special cases of the asymptotic series. They are obtained from the asymptotic series by discarding all terms of the expansion excepting the first (Doyle) or the first two (Coats–Redfern).

Generally the asymptotic series may be used for approximating integral $L(z)$ when $z > 10$. Due to rapid improvement in the approximation accuracy around $z = 10$, the boundary values for the approximation accuracy levels equal to 3%, 1% and 0.5% differ inconsiderably from one another. More accurate data are shown in Table 2. Values calculated for a given z are higher than the accurate ones ($B < 0$) when an odd number of terms of the asymptotic series are used; in the opposite case these figures are lower. The approximation accuracy of the asymptotic series rapidly increases with the increase of z and the increase in the number of expansion terms. For $z = 70$ and an expansion of eight terms, the approximation accuracy is $5 \cdot 10^{-8}$%.

It results from Table 2 that Doyle's equation is characterized by a low accuracy. Doyle's equation has an error lower than 10% for $z > 20$, and an accuracy ≤ 5% is achieved only when $z > 40$. The calculated boundary value z for the Coats–Redfern equation practically agrees with the value given by Zsakó for $B = 0.5$% [11].

Table 2

Boundary values of z for the asymptotic series for an assumed approximation error

Number of expansion terms	Approximation error not above %						Sign of error	Remarks
	3	1	0.5	0.1	0.01	0.001		
1	65.0	#	#	#	#	#	−	Doyle equation
2	14.0	24.0	34.0	#	#	#	+	Coats-Redfern equation
3	14.6	13.6	16.6	28.4	61.4	#	−	
4	9.1	10.0	12.9	18.6	32.7	58.3	+	
5	9.1	9.8	10.2	14.7	32.5	36.8	−	
6	9.2	9.8	10.0	13.9	19.3	28.2	+	
7	9.5	9.8	10.0	13.3	17.4	23.8	−	
8	9.6	9.8	10.0	12.9	15.0	20.3	+	

Bernoulli series

According to Flynn and Wall [3], the Bernoullie series may be used for = > 2:

$$L(z) \approx \frac{\exp(-z)}{z}\left(-0.0000035 - \frac{0.998710}{z} + \frac{1.98487646}{z^2} - \frac{-4.9482092}{z^3} + \right.$$

$$\left. + \frac{11.7850792}{z^4} - \frac{20.452340}{z^5} + \frac{21.1491469}{z^6} - \frac{9.5240411}{z^7} \pm 0.35 \cdot 10^{-5}\right) \quad (10)$$

The calculations carried out indicate the low usability of the Bernoulli series for the approximation of integral $L(z)$. The approximation error decreases very slowly with the increase of z and the number of expansion terms used. For $z > 15$, use of more than four terms of the expansion practically does not improve the approximation accuracy. For $z = 70$ and an eight-term expansion, the approximation error is 0.1%. The use of the Bernoulli series for $z < 9$ requires special caution, as in this range a change in the sign of error B is observed for a four and eight-term expansion. More accurate data are given in Table 3.

Table 3

Boundary values of z for the Bernoulli series for an assumed approximation error

Number of expansion terms	Approximation error not above %						Sign of error
	3	1	0.5	0.1	0.01	0.001	
1							+
2	63.5	#	#	#	#	#	−
3	14.0	24.6	37.1	#	#	#	+
4	20.0	20.0	20.0	#	#	#	+
5	7.0	9.6	12.7	#	#	#	+
6	5.0	5.0	10.0	#	#	#	+
7	5.0	5.0	9.7	#	#	#	+
8	5.0	5.0	9.7	#	#	#	+

The Vallet series

Calculating integral J [Eq. (5)], Vallet accepted other limits than those given in Eq. (6). Taking into consideration a change in the limit of integration, the equation given by Vallet [13] may be presented in the form

$$L(z) \approx L(1) + z^{-1} + \ln z - \frac{z}{1.2!} + \frac{z^2}{2.3!} + \ldots (-1)^n \frac{z^n}{n(n+1)!} - - 0.5712798419 \tag{11}$$

This series is a rapidly converging one for $z < 1$, whereas for $z > 1$ it requires a greater number of terms to be taken into account. The calculations carried out have proved the above series to be entirely useless in the approximation of integral $L(z)$ for $z > 1$.

Doyle's logarithmic equation

Doyle has reported [4] a relatively simple approximative equation in the logarithmic form:

$$\log_{10} L(z) \approx -2.315 - 0.457\, z \tag{12}$$

The calculations carried out have shown that Doyle's equation may be used for $30 \leq z \leq 45$, for which range the error $B < 3\%$. Attention must be paid to the fact that error B changes its sign within this range, which substantially reduces the accuracy of the calculation of the integral J [Eq. (5)]. The accuracy of the approximative equation $\pm 3\%$ for $20 \leq z < 60$, given by Flynn and Wall [15] refers to the approximation accuracy of $\log_{10} L(z)$ and not the $L(z)$ value itself. Doyle's equation has an approximation error of integral $L(z)$ of $B = 10.24\%$ for $z = 25$, and $B = 4.64\%$ for $z = 50$. For values of z higher or lower than the given ones, the error is substantially higher.

Zsakó's equation

Based on the tabulated data [16], Zsakó proposed an approximative equation of a relatively simple form [11]:

$$L(z) \approx \frac{\exp(-z)}{(z-d)(z+2)} \tag{13}$$

where

$$d = \frac{16}{z^2 - 4z + 84} \tag{14}$$

According to Zsakó [11], the approximation accuracy of integral $L(z)$ is greater than 0.5% for $1.6 \leq z \leq 18$.

The calculations carried out confirmed Zsakó's opinion on the accuracy of approximation by Zsakó's equation of the temperature integral $L(z)$. The approximation error is positive within the entire investigated range of the z. Values calculated from Eq. (3) are below than accurate D values. The approximation accuracy increases with the increase of z, and for $z = 70$, $B = 0.07\%$. Within the entire examined z variability range, $B < 0.5\%$. More accurate data are given in Table 4.

Table 4

Boundary values of z for the Zsakó equation for an assumed approximation error

Ordinal number	Approximation error not above %						Sign of error
	3	1	0.5	0.1	0.01	0.001	
1	1.0	1.0	1.0	35.0	#	#	+

Conclusion

The calculations carried out made it possible to evaluate the accuracy of the different equations approximating the temperature integral $L(z)$ at present applied. Data given in Tables 1–4 designate the applicability limits of the individual approximative equations in relation to the assumed calculation accuracy. Taking advantage of the above-mentioned data, attention must be paid to the question of whether the given approximative equation underrates or overrates the value of the temperature integral. In a given cycle of calculations it is recommended to use equations of the same sign of error B, as otherwise the calculation accuracy may be substantially lowered.

Of the analyzed equations, merely Schloemilch's and the asymptotic series guarantee a high approximation accuracy, the accuracy of the Schloemilch series always being higher than that of the respective asymptotic series. The accuracy of the Turner – Schnitzer – Gorbachev equation is higher than that of the Coats – Redfern equation. For $z > 10$, the accuracy of an eight-term Schloemilch expansion is equal to that of Doyle's tables. Two other analyzed series, i.e. the Bernoulli and Vallet series, are not very useful in the approximation of the temperature integral. The accuracy of Bernoulli series is not high, despite the high accuracy of the numerical coefficients of the individual terms of the series. The approximation error of the Vallet series increases very rapidly so that it cannot be used in calculations for $z > 1$.

A relatively high approximation accuracy within a wide range of z is assumed by Zsakó's approximative equation. For $z > 18$ its accuracy is comparable with that of the Turner – Schnitzer – Gorbachev equation; for lower z values, on the other hand, the accuracy of the Zsakó equation is higher. Due to its simple form, the high approximation accuracy within a wide range of z values, the equation is very convenient for calculation purposes, especially by means of small pocket computers.

Doyle's logarithmic equation, on the other hand, should be used with great care. An approximation error of the temperature integral of lower than 3%is achieved with this equation only when $30 \leq z \leq 45$, this range being characterized by a change in sign of error B. This error should thus be used merely in assessment calculations.

From among the above equations, the Schloemilch equation should be used for very accurate calculations. Rapid calculations, on the other hand, require the use of Zsakó's equation, which is more convenient for these purposes.

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RÉSUMÉ — Dans cette publication, on a cherché à évaluer l'exactitude des équations permettant d'atteindre par différentes approximations l'intégrale de température. On a étudié en particulier la possibilité d'utiliser à des fins d'approximation, les méthodes de Schloemilch, Bernoulli, Vallet, Doyle, Zsakó, Coats-Redfern et Turner—Schnitzer—Gorbachev. On donne les valeurs aux limites de "z", au-dessus desquelles l'exactitude de l'approximation d'une équation donnée est supérieure ou égale à celle qui est supposée.

ZUSAMMENFASSUNG — Es werden die Auswertungsergebnisse der Annäherungsgenauigkeit des mittels verschiedener Annäherungsgleichungen erhaltenen Temperaturintegrals gegenübergestellt. Die Anwendbarkeit für Näherungszwecke der Schloemilch-schen, der asymptotischen, der Bernoulli-schen und der Vallet-schen Serien wird in Abhängigkeit von der Zahl der bei den Berechnungen gebrauchten Expansionsausdrücke und von der logaritmischen Gleichung von Doyle, sowie von den Gleichungen von Zsakó, Coats-Redfern und Turner—Schnitzer—Gorbatschev bewertet. Grenzwerte von "z", über welchen die Näherungsgenauigkeit einer gegebenen Gleichung höher oder gleich der angenommenen ist, werden gegeben.

Резюме — В статье представлены результаты вычисления приближенной точности температурного интеграла, полученного с помощью различных приближенных уравнений. Была оценена пригодность для приближенных целей серий Шломилха, асимптотических, Бернулли и Валлета в зависимости от числа расширенных выражений, используемых в вычислениях и в логарифмическом уравнении Дойли, уравнениях Жако, Коутса—Редферна и Турнер—Шнитцер—Горбачева. Даны граничные значения «z», выше которых приближенная точность данного уравнения выше или равна допускаемому.