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Accuracy of Various Approximations to the Exponential Integral in Glow Curve Theory

M. BALARIN

Akademie der Wissenschaften der DDR, Forschungsbereich Physik, Kern- und Werkstoffwissenschaften, DDR-8027, Dresden, German Democratic Republic

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The integral (1), or in generalized, dimensionless form (5), is discussed with respect to thermal activation analysis. In this field of application it is appropriate to use $y = kT/E$ as the independent variable, which is physically restricted to values $y < 0.1$. The second parameter r, attributed to a minor correctional temperature dependence of the frequency factor, is considered as a family parameter. For the evaluation of activation energy from experimental glow curve data a special factor within the integral, called slope factor $\eta_r(y)$, is required to high accuracy. For this special factor intrinsic recurrence relations with respect to r are given so that numerical basis values for $\eta_0(y)$ allow the calculation of $\eta_r(y)$. Some points for $\eta_0(y)$ are tabulated to an accuracy 9*D*. These points compare favourably with the rational approximations given by various authors, and the derivation of some modified new approximations, designed for relative accuracies of $\sim 10^{-6}$ to 10^{-3}. For numerical determination of $\eta_0(y)$, where $0 < y < \frac{1}{15}$, the algorithmic approximations $\eta_c(y)$ (Table I) and formulas VI, II, V, and IV (Table II) in the accuracy range 10^{-5} to 10^{-7} are recommended. In the range 10^{-3} the semi-empirical formulas (Table V) are sufficiently accurate, especially $\eta_0^*(y; A')$ and $\eta_0^*(y; B')$.

INTRODUCTION

Recent interest in a highly accurate, rational computation of the integral

$$\int_{T_0}^{T} T'^r \cdot e^{-E/kT'} \cdot dT' = F(T; E, r) - F(T_0; E, r) \tag{1}$$

can be observed [1–13]; T—temperature, k—Boltzmann-constant, E—activation energy. This interest is connected with improved automatization, exactness of apparatus, and experimental developments in the field of glow curve analysis as well as for similar thermostimulated physical, electronical, and chemical kinetic processes.

In thermoanalytical experiments a reaction is systematically enhanced by steadily raising the temperature in order to locate the temperature region where traceable reaction progresses with a maximum of the reaction velocity at a distinct $\bar{T}$, followed by an exhaustion of still unreacted partners. In the result, the following kinetic parameters are estimated quantitatively:

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E—activation energy,

K—frequency factor,

1—kinetic order, and

r—temperature exponent of the frequency factor.

The corresponding differential equation is

$$-dC/dT = (K_0/q) \cdot C^l (T/\bar{T})^r \cdot e^{-E/kT}; \qquad C(T_0) = C_0, \tag{2}$$

C—concentration of reactants, $q = dT/dt$—heating rate. In previous literature, except [1, 12], only the case $r = 0$ has been considered. A more general solution will now be derived.

From a data plot $C(T; q)$ under these thermostimulated conditions the value of the activation energy can be determined by means of a well-known integral method [14–16] leading to a line of the "concentration" integral versus reciprocal temperature with the slope

$$\frac{d}{d(1/kT)} \left(-\int_{C_0}^{C(T)} \frac{dC}{C^l} \right) = \frac{d \ln F}{d(1/kT)} = -\frac{E}{\eta_r(kT/E)}. \tag{3}$$

The slope factor, $\eta_r(kT/E)$, is very close to unity and varies extremely slowly and montonically as the argument $y \equiv kT/E$ increases. This factor completes integral (1), namely,

$$F(T; E, r) = \eta_r \cdot e^{-E/kT} \cdot kT^{2+r}/E = \eta_r \cdot y^2 \cdot dF/dy. \tag{4}$$

Several values of $\eta_0(y)$, significant to $9D$, are tabulated for $0 < y < 0.5$ (column 4, Table I).

The usefullness of the special function $\eta_r(y)$ will be discussed with respect to thermal analysis. Corresponding recurrence relations and inequalities as well as likely approximations will be proposed. Relations to other special and tabulated functions [17–28] will be shown.

Before going into a detailed description of the special function $\eta_r(y)$ a few words on the philosophy of approximations in view of the availability of high speed computing machinery shall be cited from the preface of Luke's "Mathematical Functions and Their Approximations" [21]:

> To impress tables in the memory of a computer and then program for table look up and interpolation is not economical. A computer requires efficient algorithms and schemes for the evaluation of functions on demand. Numerical values of functions are but a facet of the overall problem. We desire approximations to complete functions and their zeros, to simplify mathematical expressions such as integrals and transforms, and to facilitate directly the mathematical solution of a wide variety of functional equations such as differential equations, integral equations, etc. So the main thrusts are on the development of analytical expansions and approximations of functions for universal use.

TABLE I

Values of the Function $\eta_0(y)$ Accurate to about 9D

1	2	3	4	5	6	7	8	9	10	11	12	13
				$\eta_A(y)$ [11] =	$\eta_B(y) =$	Deviation $D \equiv \Delta\eta_0^*/\eta_0 = (\eta_0^* - \eta_0)/\eta_0$ in ppm for η_0^* =						
X	$\langle y \rangle$	$I(y;0)$	$\eta_0(y)$	$(1+4y)^{-1/2}$	$(1+4y+8y^3)^{-1/2}$	η_A	η_B	η_C	$\eta_0^{(2)}$	$\eta_0^{(3)}$	$\eta_0^{(4)}$	$\eta_0^{(5)}$
∞	0.0	0.0	1.00000000	1.000000	1.000000	0	0	0	0	0	0	0
100	0.010	0.36478E–47	0.980577130	0.980581	0.980577	4	–0	1	23	–1	0	–0
90	0.01111	0.98984E–43	0.978487310	0.978492	0.978487	5	–0	1	32	–2	0	–0
80	0.01250	0.27521E–38	0.975893357	0.975900	0.975893	7	–1	1	45	–3	0	–0
70	0.01429	0.78908E–34	0.972587700	0.972598	0.972587	10	–1	2	67	–5	0	–0
60	0.01667	0.23551E–29	0.968230650	0.968246	0.968229	16	–2	3	106	–9	1	–0
50	0.020	0.74236E–25	0.962225175	0.962250	0.962222	26	–3	4	182	–18	2	–0
45	0.02222	0.13546E–22	0.958281012	0.958315	0.958276	35	–5	5	248	–27	4	–1
40	0.0250	0.25315E–20	0.953415872	0.953463	0.953408	49	–8	6	350	–43	6	–1
35	0.02857	0.48756E–18	0.947263835	0.947331	0.947252	71	–13	8	519	–72	12	–2
30	0.03333	0.97656E–16	0.939235116	0.939336	0.939214	108	–23	10	814	–132	26	–6
25	0.040	0.20628E–13	0.928313225	0.928477	0.928272	176	–45	11	1386	–268	62	–17
20	0.05	0.47024E–11	0.912581800	0.912871	0.912491	317	–100	4	2650	–638	184	–62
15	0.06667	0.12072E–08	0.887937199	0.888523	0.887693	660	–275	–41	6077	–1931	738	–330
10	0.10	0.38302E–06	0.843666606	0.845154	0.842750	1763	–1087	–376	19360	–9087	5136	–3398
8	0.1250	0.42672E–05	0.814103085	0.816497	0.812277	2940	–2243	–955	36417	–21162	14825	–12165
6	0.16667	0.53043E–04	0.770365349	0.774597	0.766131	5493	–5497	–2783	81738	–62494	57699	–62494
4	0.250	0.79956E–03	0.698469602	0.707107	0.685994	12366	–17861	–10559				
2	0.50	0.18767E–01	0.554685532	0.577350	0.500000	40861	–98588	–69026				

Note. These values are the basis for the numerical comparison of all other approximative formula. Notice the slow monotonic diminution of $\eta_0(y)$ and the considerable increase of the order of magnitude of $I(y;0)$ with increasing y. For η_A, η_B, η_C, $\eta_0^{(N)}$—see text!

And especially for polynomial and rational approximations cited striking virtues are "that they have better convergence properties than their Taylor series counterparts," that they "satisfy simple recursion formulas, which can be used in the forward direction to generate values of the polynomials," and that they "give rise to two-sided inequalities for these functions."

Physical Background and Parameter Range

Reactions always take place at temperatures $T \ll E/k$, with physical dimensions: E in electron volts, T in degrees Kelvin, at: $T[\mathrm{K}] \ll 11604.5 \cdot E[\mathrm{eV}]$. At very low temperatures the reaction is "frozen in." Depending on the sensivity of measuring equipment certain reactions can be traced when T is raised to some $(\frac{1}{50} \cdots \frac{1}{40}) \cdot E/k$. Maximum velocities are reached at $\bar{T} \sim (\frac{1}{30} \cdots \frac{1}{15}) \cdot E/k$; this moment is, to a minor part, also dependent on the amount of the frequency factor K_0, but practically independent both on r and l. A very rough estimate from the maximum condition is

$$\bar{T} \cong \frac{E/k}{\ln(10^4 K_0/q) - 2\ln(\ln(10^4 K_0/q))}.$$

A reaction peak at $\bar{T}$ has a finite half-width [24, 25]

$$\delta \cong 2.3 \cdot \bar{y} \cdot \bar{T} \simeq 0.1\bar{T},$$

so that for $T < 0.85 \cdot \bar{T}$, essentially no reaction occurs (but here are no mathematical difficulties). For $T > 1.1 \cdot \bar{T}$ all reactants are exhausted and the reaction is finished.

A ground value for K_0 in solid state reactions is the Debye frequency of that solid $= 10^{13}$–10^{14}/s. Many reactions become perfect only after a large number of jumps of one or of all kinds of the reactants through the bulk of the material. Due to this retardation K_0 can be as low as $K_0 \cong 10^5 \cdots 10^{10} \cdots 10^{15}$ per second [24]. In all these cases, we limit our interest to values $0 < y < \frac{1}{10}$ or at least to $y < \frac{1}{15}$.

In the practice of thermal analysis single reaction processes can seldom be observed, mostly a complex spectrum appears. Some processes can proceed simultaneously or consecutively. They can influence different measureable properties with different weights. It is possible that one or all kinetic parameters are not represented by discrete values, whereas any underlying distribution for these parameters may not be known. Here our concern is with the idealized case of a single process with discrete kinetic parameters and restricted to small y.

Today a relative accuracy of the order $10^{-2\pm0.5}$ is often required for the determination of the activation energy from the analysis of kinetic reaction data; ten years ago this level was of the order 5–10%. Different analytical approximations for the function $\eta_r(y)$ with acuracies up to 10^{-6}, to be considered in this note, offer theoretical advantages for future developments.

Due to an internal compensation the relative error obtainable for the frequency factor is predetermined by $\Delta K/K = 1/\bar{y} \cdot \Delta E/E$. When a parameter evaluation is started from experimental data the most sensitive parameter is activation energy and therefore η_r is directly required in (3). The integral (1) or (5) itself is not necessary in any direct sense, although such claims are overemphasized as an unresolved problem in many thermoanalytical publications.

The temperature dependence of the reaction rate is mainly expressed by the exponential Arrhenius term $\exp(-E/kT)$; through the preexponential factor T^r a minor correctional temperature influence is taken into account. In some reaction models this factor represents temperature dependence of reaction cross sections, or reactants mobilities. Usually the power r is an integer or half-integer value. Because it reflects only a minor additional temperature influence, r is not much different from zero, e.g., $-3 < r < +3$. In this sense r is not treated as a variable, but as a family parameter.

TABLE

Comparison of Likely Approximations $\eta_0^*(y)$ to

	For I [17, 4]	I_{red}	II (see text!)	III	IV $\eta_{0,3,3}^{(6)}$
X	approximation:		$\frac{1 + 7{,}5y + 3{,}5y^2}{1 + 9.5y + 16.5y^2 + 9y^4}$	$\eta_0^{(7)} + 220800y^8$	$\frac{1 + 13y + 36y^2 + 6y^3}{1 + 15y + 60y^2 + 60y}$
	main error term:		$-6y^5$		$720y^7$
∞	−6.39	−6.40	0.0	0.0	0.0
100	−1.86	−2.01	0.00	0.00	0.00
90	−1.56	−1.72	0.00	0.00	0.00
80	−1.23	−1.40	−0.01	−0.00	−0.00
70	−0.85	−1.05	−0.01	−0.00	−0.00
60	−0.45	−0.66	−0.01	0.00	0.00
50	−0.03	−0.27	−0.03	−0.00	0.00
45	0.18	−0.06	−0.03	0.01	0.01
40	0.34	0.10	−0.08	−0.01	0.00
35	0.48	0.25	−0.16	−0.03	0.00
30	0.55	0.35	−0.34	−0.09	0.01
25	0.51	0.39	−0.85	−0.29	0.03
20	0.32	0.40	−2.52	−1.05	0.12
15	−0.01	0.59	−9.98	−0.48	0.61
10	−0.21	1.99	−63.96	404.65	5.07
8	−0.11	3.53	−169.51	3941.95	15.01
6	0.08	5.95	−562.96	60790.59	55.58

Note. Represented are the relative deviations $D \equiv \Delta\eta_0^*/\eta_0 = (\eta_0^* - \eta_0)/\eta_0$ in parts per million (ppm).

ON CALCULATIONAL PROCEDURES

Values in the tables are significant to the number of digits tabulated. Occasional calculations were made with integer values for the indicated x; $\langle y \rangle$ means a rounded value of $y = 1/x$. In all analytical representations the description by the small unrounded quantity y is prefered (not x- as was often done for other approximations [1–10, 12]—see later) to emphasize the convergence tendencies.

For systematic comparisons of various good (see Table II) and some less appropriate (Table III) approximations, relative deviations from the exact values are given in parts per million (in ppm). A thorough error estimation is required. In [4] Jenkins claims, that a given rational approximation (originally from [17]) to the Airy function (in this note later compared as approximation formula I) has for the integral $F(T; E)$ an error limitation $|\varepsilon| < 2 \cdot 10^{-8}$ for all $x \geqslant 1$. Notice that for all $x \geqslant 15$ the

$\langle y \rangle$ with a Decreasing Number of Accounted Terms

V	VI	VII	VIII	IX	X
[10]		[10]	[9]	[27,5,7,9,10]	
$\eta^{(5)}_{0,2,3}$	$\eta^{(4)}_{0,2,2}$	$\eta^{(3)}_{0,1,2}$	$\eta^{(2)}_{0,1,1}$	$\eta^{(1)}_{0,0,1}$	$\eta^{(1)}_{0,1,0}$
$\frac{1+10y+18y^2}{1+12y+36y^2+24y^3}$	$\frac{1+6y+2y^2}{1+8y+12y^2}$	$\frac{1+4y}{1+6y+6y^2}$	$\frac{1+y}{1+3y}$	$\frac{1}{1+2y}$	$=1-2y$
$-144y^6$	$48y^5$	$-12y^4$	$6y^3$	$-2y^2$	$-6y^2$
0.0	0.0	0.0	0.	0.	0.
0.00	0.01	−0.10	6.	−189.	−589.
0.00	0.01	−0.15	7.	−231.	−725.
−0.00	0.01	−0.25	11.	−291.	−915.
−0.00	0.02	−0.40	15.	−376.	−1192.
−0.00	0.05	−0.72	24.	−505.	−1615.
−0.01	0.10	−1.42	41.	−714.	−2313.
−0.00	0.18	−2.09	55.	−871.	−2844.
−0.02	0.29	−3.24	76.	−1085.	−3583.
−0.04	0.53	−5.26	110.	−1391.	−4652.
−0.08	1.06	−9.15	169.	−1847.	−6284.
−0.21	2.36	−17.42	278.	−2572.	−8955.
−0.64	6.15	−37.55	506.	−3825.	−13787.
−2.56	20.25	−97.68	1072.	−6289.	−23955.
−15.83	98.85	−347.43	2548.	−12248.	−51758.
−40.21	224.33	−667.93	5010.	−17323.	−78741.
−123.42	607.48	−1472.78	9622.	−26436.	−134610.

TABLE III

Control for Some Competitive Approximations

Author or used by	Rational Approximation $\eta_0^*(y)$	Leading Error Terms	Deviation $\Delta\eta_0^*/\eta_0$ in ppm for the Arguments: $y=\frac{1}{100}$	$\frac{1}{50}$	$\frac{1}{25}$	$\frac{1}{15}$
HASTINGS [17, 19]	$\frac{0.995924 + 1.430913y}{1 + 3.330657y + 1.681534y^2}$		−3127.	−2363.	−1257.	−381.
Modified	$\frac{1 + 1.5y}{1 + 3.5y + 1y^2}$	$5y^3 - 42y^4 \dots$	5.	33.	224.	847.
HASTINGS [17, 19]	$\frac{0.99997 + 3.03962y}{1 + 5.03637y + 4.1916y^2}$		−7.	1.	2.	0.
SQUIRE [9]	$\frac{1 + 3.0396y}{1 + 5.03637y + 4.1916y^2}$		21.	29.	27.	23.
Modified	$\frac{1 + 3y}{1 + 5y + 4y^2 + 1y^3}$	$1y^3 - 22y^4 \dots$	1.	5.	21.	29.
HASTINGS [17–19]	$\frac{0.999837 + 4.13522y + 2.23934y^2}{1 + 6.1265272y + 8.666013y^2 + 2.47663y^3}$		−88.	−41.	3.	14.
Modified	$\frac{1 + 4y + 2y^2}{1 + 6y + 8y^2 + 4y^3}$	$-16y^4 + 168y^5 \dots$	−0.	−2.	−24.	−141.

ZSAKO [8]	$\frac{1-4y+84y^2}{1-2y+76y^2+152y^3-32y^4}$	$-2y^2+36y^3\cdots$	−172.	−580.	−1522.	−2014.
Corrected β_2	$\frac{1-4y+84y^2}{1-2y+74y^2+152y^3-32y^4}$	$32y^3-276y^4\cdots$	30.	227.	1526.	5140.
Modified	$\frac{1-4y-8y^2}{1-2y-18y^2}$	$-60y^4+528y^5\cdots$	−1.	−9.	−136.	−1049.
Modified	$\frac{1-4y-8y^2}{1-2y-18y^2-42y^3}$	$18y^4-444y^5\cdots$	−0.	−3.	−33.	−145.
ROECK [12]	$\frac{1+6.055y+57.412y^2-674.567y^3}{1+8.022y-49.313y^2-841.655y^3-1699.066y^4}$	"$0.03y+117y^2\cdots$	11442.	43803.	174705.	591076.
Corrected Sign β_2	$\frac{1+6.055y-57.412y^2-674.567y^3}{1+8.022y-49.313y^2-841.655y^3-1699.066y^4}$	"$0.03y+1.9y^2\cdots$	512.	1220.	171.	−28605.
Modified	$\frac{1+6y-57y^2}{1+8y-47y^2-118y^3}$	$128y^4-660y^5\cdots$	1.	15.	214.	1474.
SENUM-YANG [10] Misprint in the original [10] $\Delta\alpha_2=2$	$\frac{1+18y+88y^2+96y^3}{1+20y+120y^2+240y^3+120y^4}$	$2y^2\cdots$	168.	573.	1717.	3405.
Simple Comparison:	$\frac{1}{1+2y-2y^2}$	$8y^3-60y^4\cdots$	7.	56.	392.	156.

Note. The relative deviations are written in the same dimensions as in Table II.

value of the integral is smaller than this error limit, decreasingly by several orders of magnitude. The relative accuracy becomes less accurate $\sim 6 \cdot 10^{-6}$ for very small y (see Table II, column 2).

THE SPECIAL FUNCTION $\eta_r(y)$

For generalization of (1) we consider in dimensionless form with $y \equiv kT/E$,

$$I(y; r) = \int_0^y y'^r \cdot e^{-1/y'} \cdot dy' = \eta_r(y) \cdot y^{2+r} \cdot e^{-1/y} \tag{5}$$

and, equivalently,

$$\eta_r(y) = \frac{e^{1/y}}{y^{2+r}} \cdot \int_0^y y'^r \cdot e^{-1/y'} \cdot dy'. \tag{6}$$

Equation (6) is a solution of a Riccati-type differential equation of first order

$$\frac{d\eta_r}{dy} + \frac{1 + (2 + r)\, y}{y} \cdot \eta_r = \frac{1}{y^2}. \tag{7}$$

From (6) it can be seen that $\eta_r(0) = 1$ and $\eta_{-2}(y) \equiv 1$. The η_r satisfy the following recursion formulas

$$\eta_{r+1}(y) = \frac{1}{r+2} \cdot \frac{1 - \eta_r}{y}, \tag{8}$$

$$\eta_{r-1}(y) = 1 - (r + 1) \cdot y \cdot \eta_r(y), \tag{8'}$$

and $\eta^{-3} = 1 + y$; $\eta^{-4} = 1 + 2y + 2y^2$; and so on. A rough two-sided enclosure is estimated to be for $y \neq 0$,

$$\frac{1}{1 + (r + 2)\, y} < \eta_r(y) < \frac{1}{1 + (r + 1)\, y} \tag{9}$$

and

$$\cdots < \eta_{r+2} < \eta_{r+1} < \eta_r < \eta_{r-1} < \eta_{r-2} \leqslant \cdots \tag{10}$$

and

$$\cdots < \eta_0 < \eta_{-1} < \eta_{-2} \equiv 1 < \eta_{-3} < \cdots .$$

Within the range $y < \frac{1}{10}$, $\eta_r(y)$ is a positive, monotonically decreasing function for all

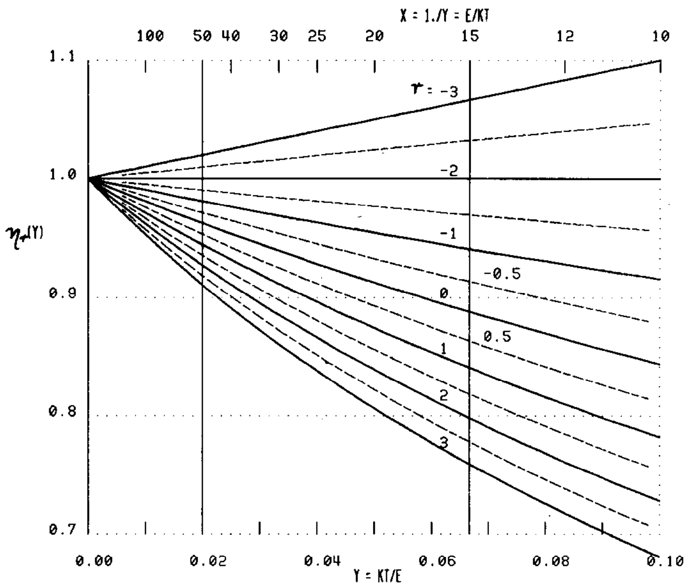

FIG. 1. Special function $\eta_r(y)$ for $0 < y < 0.1$ and $r = -3 \cdots +3$.

$r > -2$ and an increasing function for $r < -2$, as can be seen in Fig. 1. Some numerical values for the case $r = 0$ are given both for the integral $I(y; 0)$ and for the slope factor in Table I, columns 3 and 4.

SEMICONVERGENT POLYNOMIAL APPROXIMATION

Substituting $\eta_r \sim \sum_n \theta_n \cdot y^n$ in Eq. (7) leads to the known [14, 15]

$$\eta_r^{(N)}(y) = 1 + \sum_{n=1}^{N} (-y)^n \cdot (n+1+r)! \tag{11}$$

This is an alternating, semiconvergent series. An approximation to the finite, positive integral (5) by (11) is achieved by restricting $N \simeq 1/y - 2$. Here it is of great importance, that our interest is in small y (error analysis see in [3]). For $y < \frac{1}{15}$ even with few terms $N' < N$ a high accuracy can be obtained. For an example of the convergence and the alternating character of first finite, truncated series $\eta_0^{(N)}(y)$ see Table I, columns 10–13 for $N = 2$–5. Given are the relative deviations $\Delta\eta_0^*/\eta_0 = (\eta_0^* - \eta_0)/\eta_0$ from the exact value $\eta_0(y)$ in ppm.

For polynomial interrelation use

$$\eta_r^{(N)}(y) = \eta_0^{(N)}(y) + \sum_{n=1}^{N} (-y)^n \cdot \left[\frac{\Gamma(n+2+r)}{\Gamma(2+r)} - (n+1)!\right]. \tag{12}$$

Although the polynomial representation (11) is an oscillating function with N zeros, all these zeros are well outside the appointed region $y < \frac{1}{10}$. Within this region approximation (11), due to

$$\frac{d\eta_r}{dy} = -(r+2) + 2(r+2)(r+3)\,y - + \cdots,$$

confirms the monotone slope of $\eta_r(y)$.

Two simple effective approximations to $\eta_0(y)$ and inequalities are

$$\eta_A \equiv \frac{1}{\sqrt{1+4y}} < \eta_0^{(2)}; \qquad \eta_B \equiv \frac{1}{\sqrt{1+4y+8y^3}} > \eta_0^{(3)}$$

with

$$\eta_0^{(3)} < \eta_B < \eta_0 < \eta_A < \eta_0^{(2)}.$$

A good approximation to η_0 with $\Delta\eta_0^*/\eta_0 < 10^{-5}$ for all $y < 0.05$ is

$$\eta_C \equiv \frac{1}{\sqrt{1+4y+6y^3}}$$

(see columns 5–9, Table I).

Rational Approximation

Rational approximations converge sooner than polynomial approximations. For a quotient: 1 divided by a denominator, consisting in a finite number of polynomial terms, i.e., $1/\sum_n c_n y^n$, a close approximation by a corresponding Taylor series counterpart requires a greater number of terms ($Q' > Q$), theoretically an infinite number of terms. Let

$$\eta_r^{(N)}(y) = 1 + \sum_{n+1}^{N} a_{n,r} \cdot y^n \qquad (a_{n,r} \text{ from (11)}),$$

be approximated by

$$\eta_{r,P,Q} = \frac{\sum_{p=0}^{P} b_{p,r} \cdot y^p}{\sum_{q=0}^{Q} c_{q,r} \cdot y^q}, \tag{13}$$

where $b_{0,r} = c_{0,r} = 1$; $P \leqslant N$, $Q \leqslant N$.

Then for increasing p the following equations for matrix elements must be satisfied:

$$b_{p,r} - c_{p,r} = \sum_{n=0}^{p} a_{n,r} \cdot c_{p-n,r} = a_{p,r} + \sum_{n=0}^{p-1} a_{n,r} \cdot c_{p-n,r}. \tag{14}$$

In an approximation step (P) the pair of coefficients b_p and c_p is determined, but only up to their difference $b_p - c_p$, by all the preceding correct $c_{p'}$ ($p' < p$). One of these two parameters b_p or c_p can now be chosen arbitrarily. This can be continued further with freedom to fix one of the next coefficients b_{p+1} or c_{p+1} arbitrarily. In this sense there does not exist an unambiguous rational approximation to $\eta_r(y)$.

To reduce the number of coefficients and terms for $\eta^{(N)}$ up to N coefficients can be prefixed, for instance—but not necessarily—equal to zero. The rest are then determined by the set of linear equations (14). Some resulting likely rational approximations are given in Table IV.

For comparison and illustration the closeness of these approximations to $\eta(y)$ is included in Table II; only the case $r=0$ is tabulated. In practice for a definite demand on accuracy and any limited range y one can choose the corresponding formula, which leads to sufficient accuracy and with minimal required calculational effort.

Relation of $\eta_r(y)$ to Other Published Rational Approximations

Our slope factor is correlated to

$$\eta_r(y)=\frac{e^{1/y}}{y}\cdot E_{r+2}(1/y), \tag{15}$$

where E_m represents the well-known function

$$E_m(x)=\int_1^\infty \frac{e^{xt}}{t^m}\,dt; \qquad x=1/y.$$

For the exponential integral, i.e., $m=1$ and $r=-1$, various tables are available. Also some rational approximations to $E_1(x)$ are given [17–24] in the form

$$E_1(x)=\frac{e^x}{x}\cdot \sum_{n=0}^{n'} \alpha_{n'}x^{n'-n}\Big/\sum_{n=0}^{n'} \beta_n\cdot x^{n'-n},$$

usually with $\alpha_0=\beta_0=1$.

Only one relation [17, 4] will be compared explicitely, illustrating both accuracy and redundancy. This approximation formula I is characterized by $n'=4$ with the following coefficients:

	for Formula I [17, 4]			for I_{reduced}	
n	α_n	β_n	$\beta_n-\alpha_n$	$\beta_n-\alpha_n$	β_n
0	1.	1.	0.	0.	1.
1	8.57332 87401	9.57332 23454	0.99999 36053	1.0	9.5733
2	18.05901 69730	25.63295 61486	7.57393 91756	7.5739	25.633
3	8.63476 08925	21.09965 30827	12.46489 21902	12.465	21.1
4	0.26777 37343	3.95849 69228	3.69072 31885	3.7	4.

(corresponding deviations for formulas I and I_{red}—see Table II). In consequence of the recursion formula (8),

$$\eta_0(y) = \frac{1}{y} \cdot \left[1 - \frac{e^{1/y}}{y} \cdot E_1(1/y)\right] \tag{16}$$

and, with $\alpha_0 = \beta_0$,

$$\eta_0^*(y) = \frac{\beta_1 - \alpha_1 + \sum_{n=2}^{n'} (\beta_n - \alpha_n) \cdot y^{n-1}}{\beta_0 + \sum_{n=1}^{n'} \beta_n \cdot y^n}. \tag{16'}$$

The error of this approximation for small y equals

$$\frac{\Delta\eta_0^*}{\eta_0} \cong \frac{\beta_1 - \alpha_1 + (\beta_2 - \alpha_2 + 2\beta_0 - \beta_1) y + (\beta_3 - \alpha_3 + 6\beta_0 + 2\beta_1 - \beta_2) y^2 + \cdots}{\eta_0 \cdot (\beta_0 + \beta_1 y_1 + \cdots)}. \tag{17}$$

For approximation I this leads to

$$\frac{\Delta\eta_0^*}{\eta_0} = -6.4 \cdot 10^{-6} + 0.00062y - 0.021y^2 + - \cdots,$$

and particularly to

$$\frac{\Delta\eta_0^*}{\eta_0} = -6 \cdot 10^{-6} \quad \text{for} \quad y = 0,$$

$$= -2 \cdot 10^{-6} \quad \text{for} \quad y = 0.01,$$

in full agreement with Table II.

From (16) the error propagation gives $\Delta\eta_0 \cong x \cdot \Delta(E_1 e^x/x)$. Hence the absolute error for $\eta_0(y)$ (and the relative error due to $\eta \to 1$) for the same rational approximation is x times greater than the corresponding error $\Delta(E_1 \exp(x)/x)$. Only this last error is claimed [4] to be smaller than $2 \cdot 10^{-8}$.

The relative accuracy for the determination of the integral $I(y; 0)$ is closely related to the relative accuracy of the evaluated $\eta_0(y)$ and is not equal to the accuracy of the approximation to $E_1(x)$.

To get the desired accuracy of any approximation $\eta^*(y)$ it is sufficient to evaluate every term in the polynomials $\beta_n \cdot y^n$ or $(\beta_n - \alpha_n) y^n$ accurately to within that error limit. In this sense all coefficients in formula I contain extra digits. Therefore these coefficients have been rigorously truncated to the values in the last columns (for $I_{reduced}$). The resulting $\Delta\eta^*$-deviations can be found in Table II, column 3, with no qualitative difference or disadvantage, especially for $y \leqslant \frac{1}{20}$.

Starting from the numerical redundant formula I, a still simpler expression with extremely truncated β_n and $(\beta_n - \alpha_n)$ in accordance with (14) and favourably with respect to (17) is

$$\eta_0^*(y) = \frac{1 + 7.5y + 3.5y^2}{1 + 9.5y + 16.5y^2 + 9y^4} \qquad \text{(as formula II).}$$

Here the correct trend for extremely small y to $\eta(0) = 1$ should be noticed—see Table II.

There are further approximations to the integral $I(y; 0)$ or to $E(x)$ with decimal coefficients, but commonly less accurate. They all can be treated in the same way to obtain a unified form like (13) and (16′). From this unified form and from (17) due to the smallness of the accounted y it can be estimated, to what extent the accuracy of the coefficients of the ascending power terms can be diminished. In practice this situation is not obvious; an unfortunate example is the proposal by Roeck [12], who did not give reasons for the special selection of his series coefficients (Table III).

This note discourages any further use of such alternative approximation formulas, because there are the likely approximations according to (14) and compared in Table II, especially formulas IV, V, VI, and II, with integer-like coefficients and the minimal number of terms for a distinct required accuracy.

Thermoanalytical results not obtained by our approximations should be reanalyzed for correctness of results. To promote such a revision for some often-used approximations their deviation from the correct $\eta(y)$ is given in Table III for only a few argumental points $y = \frac{1}{100}, \frac{1}{50}, \frac{1}{25}$, and $\frac{1}{15}$. For some of the original versions a modified formula shows, that the same, or even a better approach, can be found by a likely simpler expression. Some indicated formula corrections, according to (14), remove obvious misprints in the corresponding original papers.

Semi-empirical Approximation to $\eta_r(y)$

Finally a very easy approximation will be demonstrated, which is suitable when an accuracy of the order $\Delta\eta_r^*/\eta_r \simeq 0.1\%$ only is required within a strongly limited region for the argument y. From known exact reference points in the vicinity of any given argument y a linear, quadratic, or hyperbolic approach is sufficient:

$$\eta_r(y) = 1 - Ay + A'y^2 \tag{18}$$

$$= \frac{1}{1 + By - B'y^2}. \tag{18′}$$

The resulting coefficients, for instance,

$$A'(y; r) = \frac{\eta_r(y) - 1 + (2 + r)y}{y^2} \qquad \text{for} \quad A = 2 + r,$$

TABLE IV

Rational Approximations to $\eta_r(y)$; with N Highest Coefficients Prefixed to Zero

N	Prefixed Coefficients and Terms	Approximation $\eta^{(N)}_{r,p,q}(y)$	Leading Error Term $\Delta\eta^{(N)}_{r,p,q}$ For $\eta^{(N)}_{r,p,q}$	Leading Error Term $\Delta\eta^{(N)}_{r,p,q}$ For $\eta^{(N)}_{o,p,q}$
2	$b_2 = c_2 = 0$	$\eta^{(2)}_{r,1,1} = \dfrac{1 + 1y}{1 + (r+3)y}$	$= (r+2)(r+3)y^3$	$= 6y^3$
3	$b_3 = b_2 = 0$, $c_2 = 0$	$\eta^{(3)}_{r,1,2} = \dfrac{1 + (r+4)y}{1 + 2(r+3)y + (r+2)(r+3)y^2}$	$= -2(r+2)(r+3)y^4$	$= -12y^4$
4	$b_4 = b_3 = 0$, $c_4 = c_3 = 0$	$\eta^{(4)}_{r,2,2} = \dfrac{1 + (r+6)y + 2y^2}{1 + 2(r+4)y + (r+3)(r+4)y^2}$	$= 2(r+2)(r+3)(r+4)y^5$	$= 48y^5$
5	$b_5 = b_4 = b_3 = 0$, $c_5 = c_4 = 0$	$\eta^{(5)}_{r,2,3} = \dfrac{1 + 2(r+5)y + (r+8r+18)y^2}{1 + 3(r+4)y + 3(r+3)(r+4)y^2 + (r+2)(r+3)(r+4)y^3}$	$= -6(r+2)(r+3)(r+4)y^6$	$= -144y^6$
6	$b_6 = b_5 = b_4 = 0$, $c_6 = c_5 = c_4 = 0$	$\eta^{(6)}_{r,3,3} = \dfrac{1 + (2r+13)y + (r+11r+36)y^2 + 6y^3}{1 + 3(r+5)y + 3(r+4)(r+5)y^2 + (r+3)(r+4)(r+5)y^3}$	$= 6(r+2)(r+3)(r+4)(r+5)y^7$	$= 720y^7$

TABLE V

Simple Semi-Empirical Approximations

	$\eta_0^*(y;1)=1-Ay$		$\eta_0^*(y;1')=1-2y+A'y^2$		$\eta_0^*(y;B)=\frac{1}{1+By}$		$\eta_0^*(y;B')=\frac{1}{1-2y+B'y^2}$	
X	$A=\frac{1-\eta_0}{y}$	$D(A=1.8)$	$A'=\frac{\eta_0-1-2y}{y^2}$	$D(A'=5.2)$	$B=\frac{1-\eta_0}{y\cdot\eta_0}$	$D(B=1.9)$	$B'=\frac{1-\eta_0+2y\cdot\eta_0}{y^2\cdot\eta_0}$	$D(B'=1.7)$
100	1.942	1451.	5.771	−58.	1.981	793.	1.924	−22.
80	1.929	1646.	5.717	−83.	1.976	930.	1.906	−31.
60	1.906	1827.	5.630	−123.	1.969	1110.	1.878	−48.
50	1.889	1845.	5.563	−151.	1.963	1212.	1.856	−60.
40	1.863	1662.	5.465	−174.	1.954	1299.	1.824	−74.
30	1.823	814.	5.312	−132.	1.941	1282.	1.773	−77.
25	1.792	−337.	5.196	7.	1.931	1136.	1.736	−53.
20	1.748	−2829.	5.033	458.	1.916	723.	1.683	38.
15	1.681	−8939.	4.786	2073.	1.893	−409.	1.604	380.
10	1.563	−28052.	4.367	9878.	1.853	−3948.	1.470	1946.

Note. Coefficients $A(y)$, $B(y)$, etc., and the corresponding deviations $D=\Delta\eta_0^*/\eta_0$ (in ppm). If desired, the choice of the approaching coefficients can be performed at an other point $\hat{y}$; here $\hat{y}=\frac{1}{25}$.

for the case $r = 0$ are given in Table IV; the relative shift of these coefficients is small. In the neighboring columns the errors (in ppm) of the approximations (18, 18′), are presented.

For some test evaluation of experimental data these empirical approximations (18, (18′) give good estimates, much simpler and even more accurate than some formulas used previously in the literature (compare Tables V and III).

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