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Note

REMARKS ON "A NEW EQUATION FOR MODELLING NONISOTHERMAL REACTIONS"

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The formula proposed by Agrawal [7] for the approximation of the temperature integral in non-isothermal kinetics is shown to be less accurate than several approximations proposed earlier that are of the same complexity. The domain of applicability of 10 approximate formulae is discussed.

In nonisothermal kinetics of heterogeneous processes, both chemical and physical ones, the rate of the process, defined as $d\alpha/dt$, where α is the transformation degree and t is time, is presumed to be a unique function of α and of the temperature-dependent rate constant, obeying the relation

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

For the temperature-dependence of k, the validity of the Arrhenius equation

$$k = A\exp(-E/RT) \tag{2}$$

is generally presumed, where A is referred to as the frequency factor and E as the activation energy, though their physical significance is rather obscure [1, 2].

Through use of a linear temperature programme with constant heating rate, $q = dT/dt$, combination of Eqs (1) and (2) gives

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q}\exp(-E/RT)\,dT \tag{3}$$

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If it is presumed that A, E and $f(\alpha)$ do not change throughout the process, Eq. (3) may be integrated between the transformation degree limits 0 and α and the temperature limits T_0 and T, or. if the rate of the process has vanishing values at the initial temperature T_0, between the limits 0 and T:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{q} \int_0^T \exp(-E/RT)\, dT \tag{4}$$

The right-hand side of Eq. (4) is not integrable analytically. If the variable $x = E/RT$ is introduced the temperature integral becomes

$$\int_0^T \exp(-E/RT)\, dT = \frac{E}{R} \int_x^\infty x^{-2} \exp(-x)\, dx = \frac{E}{R} p(x) \tag{5}$$

If the left-hand side integral of Eq. (4) is denoted by $g(\alpha)$, we may write

$$g(\alpha) = \frac{AE}{Rq} p(x) \tag{6}$$

which is the equation of TG curves proposed by Doyle [3].

In nonisothermal kinetics, and especially in the kinetic analysis of thermogravimetric data, Eq. (6) is frequently used to test the validity of various kinetic equations, i.e. of functions $f(\alpha)$, and to derive apparent activation energies from thermal analysis data. For this purpose a great variety of methods have been proposed, based on different approximations of the exponential integral $p(x)$ [2, 4] or on the use of the numerical values of the latter, given in mathematical tables, e.g. [5, 6].

The mathematically most objectionable methods approximate the function $1/T$ to make the exponential integral analytically integrable. Better results are obtained with approximate formulae of $p(x)$, obtained either by means of different expansion procedures, or empirically. The former always give decreasing errors with increasing x, while the latter may give positive errors in some x ranges and negative ones in other domains. Most frequently, the exponential integral is approximated by means of a rational expression, multiplied by e^{-x}:

$$p(x) = \frac{q(x)}{r(x)} e^{-x} \tag{7}$$

where $q(x)$ and $r(x)$ are polynomials in x. The degree of a rational approximation may be defined as the degree of the highest degree polynomial between $q(x)$ and $r(x)$.

In a recent paper, Agrawal [7] proposes an empirical-type rational approximation, claiming that it "is more accurate than previously known approximations".

Without pretending to give a full review of the approximations proposed, I shall deal with some of them, given in Table 1.

Approximations 1–5 are those mentioned in [7], but approximations 6–10 are ignored by Agrawal. All these approaches are rational ones, except approximation 7. In order to give a clear picture of the accuracy of the approximations, the relative errors, Δ, expressed in %, are given as functions of x in Fig. 1, a double logarithmic plot being performed, as in [7]. In this plot, the horizontal straight line at $\Delta=0$ corresponds to an error of less than 0.01%.

In thermal analysis problems, an approximation of $p(x)$ ensuring an error of less than 1% may generally be considered to be sufficiently accurate. Therefore, the region corresponding to $|\Delta|<1\%$ is delimited in Fig. 1 by two horizontal dashed

Table 1 Approximations proposed for the exponential integral $p(x)$

Approximation	Degree	$p(x)$	References
1	2	$e^{-x}\frac{1}{x^2}$	[3], [7], [8], [9]
2	3	$e^{-x}\frac{x-2}{x^3}$	[3], [7], [8], [9], [10], [11], [12]
3	2	$e^{-x}\frac{1}{x(x+2)}$	[7], [9], [12], [13], [14] [15], [16], [17]
4	3	$e^{-x}\frac{x-2}{x(x^2-6)}$	[7], [18]
5	3	$e^{-x}\frac{x-2}{x(x^2-5)}$	[7]
6	3	$e^{-x}\frac{x+4}{x(x^2+6x+6)}$	[12], [13]
7	—	$e^{-x}\frac{1}{x\sqrt{x^2+4x}}$	[9]
8	4	$e^{-x}\frac{x^2-4x+84}{(x+2)(x^3-4x^2+84x-16)}$	[19]
9	4	$e^{-x}\frac{x^2+10x+18}{x(x^3+12x^2+36x+24)}$	[12], [13]
10	3	$e^{-x}\frac{0.995924x+1.430913}{x(x^2+3.330657x+1.681534)}$	[12], [20]

Table 2 Minimum x values for which different approximations give an absolute deviation less than the indicated value

Approximation	Δ, %		
	10	1	0.3
1	19.6	198	666
2	6.92	23.5	43.7
3	1.95	11.3	21.4
4	4.47	9.78	14.0
5	3.30	5.25	6.25
6	0.48	2.62	4.37
7	1.04	4.47	7.55
8	0.66	1.32	1.66
9	0.19	1.25	2.05
10	0.03	0.36	0.54

lines. This means that, if the Δ *vs.* x curve of the approach is situated in this region, it can be used in nonisothermal kinetics. The minimum x values for which the above condition is satisfied are indicated in Table 2. The same Table also contains the minimum x values for which $|\Delta| < 10\%$ and $|\Delta| < 0.3\%$, respectively.

Obviously, Agrawal's approach is better than approximations 1–4 are, but approximations 6 and 8–10 are much better than Agrawal's.

Approximations 1 and 2 were obtained by means of asymptotic expansion of the exponential integral $p(x)$, by truncating the series after the first and the second terms, respectively. The asymptotic expansion

$$p(x) = \frac{e^{-x}}{x^2}\left[1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \ldots + (-1)^n \frac{(n+1)!}{x^n} + \ldots\right] \tag{8}$$

is very good for $x > 50$ [22], but for small x values it may even be divergent [21]. If the first 10 terms are retained, errors will be less than 0.01% for $x > 15$, but for $x = 10$ the error already exceeds 0.2%. The error can be reduced by a factor of about 100 by adding half of the next term of the asymptotic expansion to the series [23].

Schlömlich's expansion [17]·

$$p(x) = \frac{e^{-x}}{x(x+1)}\left[1 - \frac{1}{x+2} + \frac{2}{(x+2)(x+3)} - \frac{4}{(x+2)(x+3)(x+4)} + \ldots\right] \tag{9}$$

is much better. It is convergent and, if the first two terms are retained, approximation 3 is obtained.

Inspection of Table 2 and Fig. 1 shows that, from the non-empirical-type rational approximations of the same degree, those given by Luke [13] are the best, i.e. approximations 3, 6 and 9. On comparing these approximations with the empirical

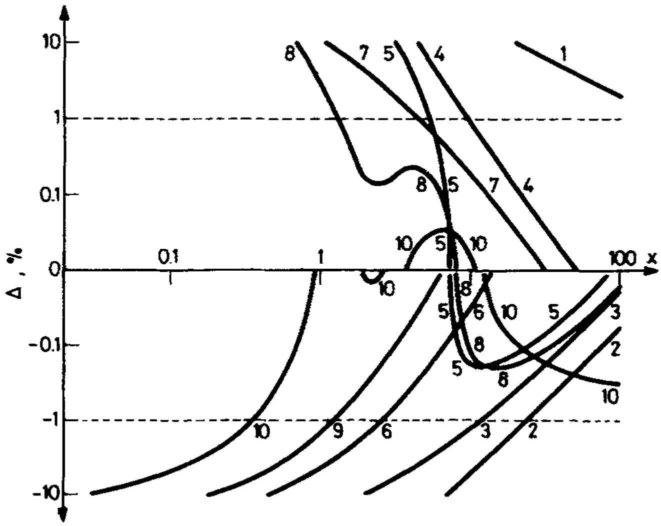

Fig. 1 Errors given by the approximate formulae presented in Table 1 for the exponential integral $p(x)$

ones, viz. with 5, 8 and 10, one must take approximations of the same degree. Both 8 and 9 are fourth degree rational approximations and 9 is generally better than 8, except in a very narrow x range, $1.38<x<2.82$, in which 8 gives lower errors than 9.

Approximations 5, 6 and 10 are all of third degree. Obviously, 6 is much better than Agrawal's empirical formula for all x values. Approximation 10 gives excellent results: the lower limit of x for which errors do not exceed 1% is reduced by a factor of more than 14 as compared to Agrawal's approach.

Consequently, the formula proposed by Agrawal is not competitive with some other known formulae of the same complexity. The problem of the exponential integral $p(x)$ generally can be considered as being solved satisfactorily. Even if the approximations given in Table 1 were not accurate enough in certain special thermal analysis problems, it would always be possible to use the power series expansion:

$$p(x) = \frac{e^{-x}}{x} + \gamma + \ln x + \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{n\,n!} \tag{10}$$

where γ is the Euler–Mascheroni constant (0.5772156649), and truncate the series at the desired accuracy [6, 12].

References

1 J. Zsakó, J. Thermal Anal., 5 (1973) 239.
2 J. Zsakó, in "Thermal Analysis" (Ž. D. Živkovič, ed.) Collection of Papers, Bor, Yugoslavia, 1984, p. 167.
3 C. D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
4 J. Šesták, Silikaty, 11 (1967) 153.
5 E. Jahnke and F. Embde, "Tables of Higher Functions", Leipzig, 1960.
6 M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", Dover Publ., New York, 1972.
7 R. A. Agrawal, J. Thermal Anal., 32 (1987) 149.
8 C. D. Doyle, Nature, 207 (1965) 290.
9 M. Balarin, J. Thermal Anal., 12 (1977) 169.
10 P. Murray and J. White, Trans. Brit. Ceram. Soc., 54 (1955) 204.
11 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
12 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1977) 445.
13 Y. L. Luke, "Mathematical Functions and Their Approximations" Academic Press Inc., New York, 1975, Chapter 13.
14 V. M. Gorbachev, J. Thermal Anal., 8 (1975) 585.
15 R. C. Turner and M. Schnitzer, Soil Sci., 93 (1962) 225.
16 R. C. Turner, I. Hoffmann and D. Chen, Canad. J. Chem., 41 (1963) 243.
17 O. Schlömlich, "Vorlesungen über höheren Analysis", Braunschweig, 1984, p. 266.
18 C. H. Li, AIChEJ., 31 (1985) 1036.
19 J. Zsakó, J. Thermal Anal., 8 (1975) 593.
20 E. Hastings "Approximations for Digital Computers", Princeton, 1955.
21 J. R. Biegen and A. W. Czanderna, J. Thermal Anal., 4 (1972) 39.
22 J. Saint-Georges and G. Garnaud, J. Thermal Anal., 5 (1973) 599.
23 R. Chen, J. Thermal Anal., 6 (1974) 585.