Note

Accurate determination of a modified exponential integral, with speciial reference to thermal analysis

A. VAN TETS

Atomic Energy Board, Private Bag X256, Pretoria 0001 (Republic of South Africa)
(Received 22 April 1976)

The differential equation

$$f(\alpha)\,d\alpha = A_0 \exp\left(-\frac{E_a}{RT}\right)dt \tag{1}$$

is of prime importance in thermal analysis. The left-hand side of eqn (1) should correspond to a reproducible kinetic model, and the right-hand side to an Arrhenius type of temperature dependence in a chemical process. To eliminate the frequency factor A_0, which depends on a kinetic model to be chosen, eqn (1) may be normalised to

$$\frac{f(\alpha)}{f(\tfrac{1}{2})} = \exp\left(\frac{1}{R}\,\Delta\,\frac{E_a}{T}\right)\cdot\left(\frac{d\alpha}{dt}\right)_{\alpha=\tfrac{1}{2}}\cdot\frac{dt}{d\alpha} \tag{2}$$

with

$$\Delta\frac{E_a}{T} = \left(\frac{E_a}{T}\right)_{\alpha=\tfrac{1}{2}} - \frac{E_a}{T} \tag{2a}$$

taking the kinetic data at halfway conversion ($\alpha = \tfrac{1}{2}$) as a standard.

Obviously, it is simple to determine the normalised kinetic function $f(\alpha)/f(\tfrac{1}{2})$ from isothermal experiments, because the temperature-dependent factor in eqn (2) can then be cancelled.

It is also possible to determine $f(\alpha)/f(\tfrac{1}{2})$ from non-isothermal experiments because the activation energy E_a can be determined independently[1] of specific kinetic models. However, to predict results with a different temperature program or to simulate thermoanalytical results, eqn (1) or (2) has to be integrated. From the conversion side, consisting of, e.g., $1/f(\tfrac{1}{2}) \int_0^\alpha f(\alpha)\,d\alpha$, integration can be carried out on a theoretical or an empirical[2] basis. Furthermore, a temperature/time relationship has to be established for this purpose.

For the widely used linear-temperature programs, dT is proportional to dt. Therefore, assuming that E_a is constant, there is considerable interest in thermal analysis for the calculation of the integral

$$E_j = \int_x^\infty x^{-2} e^{-x}\,dx = \int_0^y e^{-1/y}\,dy \tag{3}$$

with

$$x = \frac{E_a}{RT} = y^{-1} \tag{3a}$$

This integral is related to the exponential integral $-E_i(-x)$ by the formula

$$E_j = x^{-1} e^{-x} + E_i(-x) \tag{4}$$

Approximation methods have to be used to calculate integral values of this nature. In principle the series

$$E_j = c_j + x^{-1} + \ln x - \frac{x}{2!} + \frac{x^2}{2 \cdot 3!} - \frac{x^3}{3 \cdot 4!} + \ldots + \frac{(-1)^m x^m}{m(m+1)!} + \ldots \tag{5}$$

with $c_j = \gamma - 1 = -0.42278 \ldots$ \hfill (5a)

can be used for these calculations, γ being the Euler constant. However, this is not practical for $x \gg 1$, which is usually the case in thermal analysis. Many terms of eqn (5) would have to be taken for $x \gg 1$, because they only start to convert when the condition $m(m+1)/m - 1 > x$ is first met.

Approximations of E_j can also be based on the alternating series

$$E_j = x^{-2} e^{-x} (1 - 2! x^{-1} + 3! x^{-2} - 4! x^{-3} + \ldots + (-1)^n (n+1)! x^{-n} + \ldots) \tag{6}$$

of which Coats and Redfern[3] used only the first two terms in their thermoanalytical method. The accuracy of eqn (6) is limited, because the series becomes divergent in its higher terms. The higher terms of eqn (6) with $n+1 > x$ can therefore not be used for calculations.

The best series suggested in the literature for calculating E_j with $x \gg 1$ seemed to be the one proposed more than a century ago by Schlömilch[4], viz.

$$E_j \doteq x^{-1} e^{-x} \left[\frac{1}{x+1} - \frac{1}{(x+1)(x+2)} + \frac{2}{(x+1)..(x+3)} - \frac{4}{(x+1)..(x+4)} + \frac{14}{(x+1)..(x+5)} - \ldots \right] \tag{7}$$

which van Krevelen et al.[5] have used for the first time in thermal analysis. However, the first term in eqn (7) is, at least for $x > 2$, less accurate than a similar approximation formula

$$E_j \approx \frac{e^{-x}}{x(x+2)} \tag{8}$$

recently proposed by Gorbachev[6]. Although Gorbachev did show that his approximation method is more accurate than that of Coats and Redfern[3], he did not show how accurate his method actually is. It may be pointed out that the first two terms of eqn (7) taken together give exactly Gorbachev's approximation.

In the following it is proposed to use, for $x \gg 1$, the series

$$E_j = x^{-2}e^{-x}\left[\frac{x+1}{x+3} + \sum_{i=1}^{\infty} (-1)^i a_i \prod_{j=1}^{i+2} (x+j)^{-1}\right] \tag{9}$$

The first term in eqn (9) is already more accurate than eqn (8), at least for $x > 3$. In many cases it will be sufficient to use the first term in eqn (9) only. If necessary, corrections can be made by using further terms. The coefficients a_i are found by comparing eqn (6) with eqn (9), leading to

$$E_j = x^{-2}e^{-x}\left[\frac{x+1}{x+3} - \frac{6}{(x+1)(x+2)(x+3)} + \frac{30}{(x+1)..(x+4)} - \right.$$
$$\left. - \frac{108}{(x+1)..(x+5)} + \frac{810}{(x+1)..(x+6)} - ...\right] \tag{10}$$

This series converts more quickly to true integral values than the similar series in eqn (7), as is demonstrated in the Table 1 in which various calculation methods are compared numerically.

TABLE 1

APPROXIMATIONS OF $x^2e^xE_j$ WITH $x = 10$

	Terms used				
	1	2	3	4	5
eqn (6)	1.0000	0.8000	0.8600	0.8360	0.8480
eqn (7)	0.9091	0.8333	0.8450	0.8433	0.8437
eqn (8)	0.8333	—	—	—	—
eqn (10)	0.8462	0.8427	0.8439	0.8436	0.8437

REFERENCES

1 H. G. Wiedemann, A. van Tets and H. P. Vaughan, Pittsburgh Conference on Analytical Chemistry, 1966.
2 A. van Tets, Thermochim. Acta, 15 (1976) 386.
3 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
4 O. Schlömilch, Vorlessungen über höheren Analyse, Braunschweig, 2nd ed., 1874.
5 D. W. van Krevelen, C. van Heerden and F. J. Huntjens, Fuel, 30 (1951) 251.
6 V. M. Gorbachev, J. Therm. Anal., 8 (1975) 349.