THE COMPUTATION OF THE EXPONENTIAL INTEGRAL AS RELATED TO THE ANALYSIS OF THERMAL PROCESSES

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In using an asymptotic series to evaluate an exponential integral, the relative error can be reduced by about two orders of magnitude by adding one half of the smallest term. The added accuracy enables extension of the method to smaller exponents.

In a recent paper, Biegen and Czanderna [1] showed that the exponential integral used in the theory of thermogravimetry [2], thermal desorption [3], thermoluminescence (TL) [4] and thermally stimulated conductivity (TSC) [5] can be evaluated by use of an appropriate asymptotic series. The integral appearing in these theories when a linear heating rate is used is

$$\int_{T_0}^{T} \exp(-E/RT')\mathrm{d}T' \tag{1}$$

where T_0 and T are the initial and final temperatures (K), respectively, E is the activation energy (joule/mole) and R is the gas constant (joule/mole $-$ K)*.

The problem of computing the integral in Eq. (1) reduces very easily to the solution of the exponential integral, which can be given by an asymptotic series

$$E_i(-x) = \int_{x}^{\infty} (e^{-t}/t)\mathrm{d}t \sim (e^{-x}/x) \sum_{n=0} (-1/x)^n n! \tag{2}$$

A main feature of this asymptotic series is that consecutive terms alternate in sign.

The possible error made by taking m terms in the series instead of the exponential integral does not exceed the $(m+1)$th term. This explains why it should be recommended to take the terms down to that preceding the smallest term or, in other words, as mentioned by Biegen and Czanderna [1], to $n \cong x - 1$.

Chen [6] has shown that by adding one half of the next term $n \cong x$ in the series, the possible error reduces to half its previous value. In addition, Chen gave a more explicit expression for the *relative* possible error, which is now $|R_n| \approx \approx \frac{1}{2}\sqrt{2\pi x}\ \mathrm{e}^{-x}$. In a more recent paper, Chen [7] has shown, relying upon a pre-

* In TL and TSC theories, Boltzmann's constant k(ev/K) replaces R, and E is given in eV. The ratios E/kT and E/RT are, however, the same. This can be seen by multiplying both the numerator and denominator of E/kT by Avogardo's number.

vious paper by Dingle [8], that in fact the use of one half of the last term yields much better results than estimated before. The expression for the possible relative error was shown to be

$$|R_n| \approx \frac{1}{100}\sqrt{2\pi x}\,\mathrm{e}^{-x} \tag{3}$$

which is smaller by a factor of 50 than previously estimated.

Biegen and Czanderna [1] computed the value of $I(x) = \mathrm{e}^{-x}/x + E_i(-x)$ rather than the exponential integral itself. For $x = 10$ they found $I(10)$ to be 0.3822×10^{-6} with a possible relative error of $\sim 4 \times 10^{-3}$. By adding one half of the additional term we have $I(10) = 0.3830 \times 10^{-5}$. The relative error for the exponential integral in this case is $|R_{10}| = \frac{1}{100}\sqrt{2\pi x 10}\,\mathrm{e}^{-10} \approx 3 \times 10^{-6}$, corresponding to a relative error of $\sim 3 \times 10^{-5}$ in $I(10)$, and as already mentioned, this is about a hundred times better than before. For $x = 15$, the relative possible error given by Biegen and Czanderna when 16 terms are taken (which is practically the same as with the suggested 15 terms) is $\sim 4 \times 10^{-5}$. By taking only one half of the 15th term, one ends up with a relative error of $\sim \frac{1}{100}\sqrt{2\pi\, 15}\; e^{-15} \cong 3 \times 10^{-8}$ in the exponential integral, which corresponds to a relative error of $\sim 4 \times 10^{-7}$ in $I(x)$. This, again, is about a hundred times better than before. The improvement of the use of this method in the analysis of thermal reaction data is obvious. For example, the range of evaluating $I(x)$ with a reasonable possible error can be extended to values of $x = E/RT$ of 10 and less.

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