Journal of Thermal Analysis, Vol. 16 (1979) 193—195

THE ACCURACY OF EQUATIONS APPROXIMATING THE TEMPERATURE INTEGRAL. PART II

N. HAJDUK and J. NORWISZ

Institute of Non-Ferrous Metals, Gliwice, Poland

(Received December 9, 1977; in revised form August 10, 1978)

The present paper shows the results of an analysis of the approximation accuracy of the temperature integral through the logarithmic equation elaborated by MacCallum and Tanner. The accuracy of this equation is higher than that of the similar logarithmic equation presented by Doyle, although substantially lower than the accuracy of other approximative equations appearing in the literature. Due to its simple form, this equation may be used for initial and quick elaborations of results of kinetic measurements made under conditions of linear temperature increase.

In a previous study [1], the accuracy was analyzed of the most frequently applied approximative equations for the temperature integral

$$L(z) = \int_{z}^{\infty} \frac{\exp(-x)}{x^2}\, \mathrm{d}x \tag{1}$$

where

$$z = \frac{E}{RT_a} \tag{2}$$

E is the activation energy, R is the gas constant, and T_a is the final temperature. Equations of this kind are usually given in the form of a function of the independent variable z. Merely in the equation presented by MacCallum and Tanner [2]

$$\log_{10}(z) = -0.4828E^{0.4351} - \frac{0.449 + 0.217E}{T_a} 10^3 \tag{3}$$

where E is expressed in kcal/mole, the activation energy E and temperature T_a occur in an evident form. The equation as a function of $1/T_a$ describes a straight line. The equation of Doyle [3], which is shown below, has the same character:

$$\log_{10}(z) = -2.315 - 0.4567z = -2.315 - 0.4567 \frac{R}{RT_a} \tag{4}$$

The aim of the present paper is an analysis of the approximation accuracy of integral $L(z)$ through Eq. (3). The approximation error has been determined according to the equation

$$B = \frac{D - A}{D} \cdot 100\% \qquad (5)$$

where D is the accurate value of integral $L(z)$ and A is the value calculated from the approximative equation. The value of integral $L(z)$ computed numerically by means of Simpson's procedure has been assumed as the accurate value D. Error B does not exceed $1.\ 10^{-8}$ of the value of $L(z)$.

The variation range of values of the activation energy and temperature has been selected in such a way as to cover values most frequently occurring in practice. The results of calculations are shown in Table 1. Analogous calculations were performed for Eq. (4) [1].

Table 1

Approximation error for MacCallum and Tanner's equation

Temperature, K	Activation energy, kcal/mole					
	10	20	30	40	50	60
300	41.92	8.58	−9.65	−20.53	−27.48	−32.29
500	17.83	−17.36	−29.48	−31.39	−29.08	−24.36
700	22.40	−4.42	−10.29	−9.87	−3.43	3.59
900	32.47	12.18	9.64	13.84	19.22	25.97
1100	42.20	27.54	26.08	29.78	35.79	43.03
1300	50.04	39.13	38.98	42.75	48.03	53.76
1500	57.04	48.41	49.00	53.07	57.56	62.08

The approximation error is different for various activation energies and temperatures. The range, however, within which the approximation error would be very small, e.g. 0.5%, is very narrow and has no practical meaning. A superficial analysis of the data shown in Table 1 already indicates the low approximation accuracy of the temperature integral through Eq. (3). The mean value of the error is 18.16% for Eq. (3) and 38.50% for Eq. (4). The values calculated by means of Eqs (3) and (4) are lower on the average than the accurate values, the error being less for Eq. (3).

It must be added that the approximation accuracy $L(z)$ is different from that of $\log_{10} L(z)$. The approximation error has additionally been determined for a temperature of 300 K for Eq. (3), using the following relation:

$$b = \frac{\log_{10} D - \log_{10} A}{\log_{10} D} \cdot 100\% \qquad (6)$$

The value of error b was very small and varied from −2.4% to −0.2%. Such values of the approximation error have also been presented by MacCallum and Tanner [2].

The low accuracy of Eq. (3) reduces the possibility of its use in laboratory practice. However, thanks to its form, Eq. (3) may simplify to a substantial degree the method of kinetic constant determination. For this reason, it should primarily be used during initial elaboration of experimental data.

References

1. J. Norwisz and N. Hajduk, J. Thermal Anal., 13 (1978) 223.
2. I. MacCallum and P. Tanner, Eur. Polymer J., 6 (1970) 1033.
3. C. D. Doyle, J. Appl. Polymer Sci., 6 (1962) 639.