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AN APPROXIMATION TO THE LINEAR HEATING RATE IN NON-ISOTHERMAL KINETICS

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A near-linear representation of the linear heating rate is presented which converts the exponential integral into an integrable form and allows a simple determination of the activation energy to high accuracy.

The general kinetic equation in non-isothermal studies is

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = A \int_0^t e^{-E/RT}\,\mathrm{d}t \tag{1}$$

For the linear heating rate the substitution of $\mathrm{d}t = \mathrm{d}T/\phi$, and integration by parts, results in the exponential integral on the right-hand side of Eq. (1). While the approximation of this integral is possible to any desired degree of accuracy [1–4], these solutions generally require computer evaluation or tedious and inaccurate graphical techniques. Efforts to simplify the evaluation of Eq. (1) have included the imposition of non-linear heating conditions [5, 6] and the approximation of the integrand by integrable functions [7, 8]. The former method is difficult to implement and the latter can result in considerable error [9].

It is proposed here that the linear heating rate be approximated by

$$\frac{\mathrm{d}T}{\phi} \approx \frac{b}{\phi}\,\frac{T_\mathrm{m}^2}{T^2}\,e^{2(1-T_\mathrm{m}/T)}\,\mathrm{d}T \tag{2}$$

The constant T_m is the temperature at which the right-hand side of Eq. (2) is at a maximum, and the constant b, very nearly equal to one, is selected to optimize the approximation. Substitution of Eq. (2) into Eq. (1) yields

$$g(\alpha) = \frac{AbT_\mathrm{m}^2 e^2}{\phi} \int_0^T e^{-(E/R+2T_\mathrm{m})/T}\,\frac{\mathrm{d}T}{T^2} \tag{3}$$

which is readily integrated to

$$g(\alpha) = \frac{AbT_\mathrm{m}^2 e^2}{\phi(E/R + 2T_\mathrm{m})}\,e^{-(E/R+2T_\mathrm{m})/T} \tag{4}$$

A plot of log $g(\alpha)$ *vs.* $1/T$ is then a straight line of negative slope $(E/R + 2T_\mathrm{m})/2.303$.

The accuracy of the approximation is enhanced if T_m is taken near the midpoint of the temperature range and b is selected to minimize the integrated area between the left- and right-hand sides of Eq. (2) in the same temperature interval. For example, in the range $0.9 < T/T_m < 1.1$ the approximation is always within 1% of its maximum value, and thus b can be chosen such that the approximation will be within 1/2% of the inverse heating rate at any temperature in the range. Since the heating rate is merely a multiplicative factor in the integral in Eq. (3), the error analysis applies in that case as well. It is worthwhile noting that the approximation is completely determined by the temperature range and is independent of the details of the experimental data.

The activation energy determined from the slope of the log $g(\alpha)$ *vs.* $1/T$ plot is quite insensitive to the value selected for T_m. The relative variation in the activation energy caused by variation in the choice of T_m is only

$$\left|\frac{\Delta E}{E}\right| \approx \frac{2R}{E} \, |\Delta T_m| \tag{5}$$

The inherent accuracy of this method is a marked improvement over that of any previous approximation to the integrand [7, 8].

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