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Note

Generalized Solution of the Glow Curve Integral Applied to Nonlinear Heating Rates

Evaluation of the integral

$$F_t(t, E) = \int_0^t \exp(-E/kT)\, dt' \tag{1}$$

is of general importance in the interpretation of thermal disorption of gases and other "glow-curve" data [1–5]. k is the Boltzmann constant in ev per degree. Since it has been conventional to use a linear heating rate ($T = T_0 + \beta t$) to obtain data as a function of temperature, the procedure has been to factor out $1/\beta$ leaving the modified form

$$F(T, E) - F(T_0, E) = \int_{T_0}^{T} \exp(-E/kT')\, dT', \tag{2}$$

and to treat $F(T_0, E)$ as a constant when it cannot be neglected in comparison with $F(T, E)$.

Chen [1] considered the asymptotic series solution in powers of (kT/E) for $F(T, E)$ and has provided appropriate criteria for truncation and error estimation.

Redhead [3] has chosen an alternative approach which leads to a closedform solution of the original integral (1) by taking a heating rate in which the inverse temperature is linear in time. Although this may prove experimentally impractical—particularly for extended temperature intervals—it does suggest a generalized approach for nonlinear monotonic heating curves. The approach this paper offers should have special appeal for experiments where less restrictive temperature programming is desirable and it is possible to continuously monitor the time-temperature relationship.

To see the effect of various heating rates upon the integral—and to open the possibility of simplifying it by adjusting the heating rate—a general form is needed. One such general solution is obtained by using $x \equiv 1/T$ and repeatedly integrating by parts, giving

$$F_t(t, E) = [\exp(-xE/k)]\, B(x, E)|_{x=1/T_0}^{x=1/T} \tag{3}$$

where

$$B(x, E) = -\sum_{n=1}^{\infty} (k/E)^n \, d^n t/dx^n. \tag{4}$$

This will reduce to the asymptotic series treated by Chen, when the derivatives of

$$t = (1/\beta)(T - T_0) = (1/x - T_0)/\beta$$

are substituted into (4). From (4) it is now clear that Redhead's heating curve is the simplest possible, as it leaves but one term in (4). But Eq. (4) can now show the effect of a general monotonic curve—say, one resulting from a single heater power setting. A monotonic time-temperature curve may be fitted by a series, as

$$t = \sum_{j=0}^{J} b_j(10^3 x)^j, \tag{5}$$

where the b_j are evaluated from a difference table [6] of values of time taken at regular intervals of $10^3/T$. J cannot be larger than the number of data points considered. Usually a smaller value will be dictated by the noise in the data, which will overshadow the "ideal values" in the table. J is then taken as the order of difference just prior to the onset of randomness [7, p. 150]

In the experimental work prompting this investigation, for example, a single heater setting produced a temperature-time curve which required only three terms ($J = 2$) to fit a range of interest extending over some 300°K, with a maximum deviation of less than 2%. When the range of interest is smaller than the total temperature sweep, the heater setting can be chosen to optimize the shape of the sweep within that range, and so keep the number of terms small.

With t now given by Eq (5), the derivatives are

$$\frac{d^n t}{dx^n} = \sum_{j=n}^{J} 10^{3j} b_j x^{j-n} j!/(j-n)!, \tag{6}$$

and can be substituted into (4) to yield

$$B(x, E) = -\sum_{n=1}^{J} \sum_{j=n}^{J} (k/E)^n \, 10^{3j} b_j x^{j-n} j!/(j-n)! \tag{7}$$

It is useful to rearrange them into simple powers of x. Setting the terms of the double sum of (7) out with one dummy index for the row and the other for the column, it becomes clear that simple powers of x are shared by elements along diagonals. To separate these out, substitute dummy indices with m replacing $j - n$, yielding

$$B(x, E) = -\sum_{m=0}^{J-1} (10^3 x)^m \left\{ \sum_{j=m+1}^{J} b_j (10^3 k/E)^{j-m} j!/m! \right\}. \tag{8}$$

Given the value of E, the set of factors in the brackets may be evaluated once, and treated as constants. On the other hand, in situations where E is being sought by some iteration process performed upon the data as analyzed by Eq (1), a useful first step is to treat $10^3 k/E$ as small (note $10^3 \mathrm{k}/E \approx .1$ when E is in the one ev range), neglect higher powers, and factor the unknown E out into the preexponential constant. Plots so made could furnish a good zero-th order value for E.

In conclusion, this paper has offered a more general solution to the integral of Eq (1), and a method of applying that solution to general, monotonic heating curves. Thus, even a curve generated by a single heater power setting may result in a finite series solution of only two or three terms.

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