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USE OF ASYMPTOTIC ANALYSIS OF THE LARGE ACTIVATION-ENERGY LIMIT TO COMPARE GRAPHICAL METHODS OF TREATING THERMOGRAVIMETRY DATA

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ABSTRACT

An earlier numerical analysis showed that the second approximate method of Horowitz and Metzger can be rendered exceedingly accurate for reduction of thermogravimetry data. It is demonstrated here that this result can be justified on the basis of an asymptotic expansion with a nondimensional activation energy as the large parameter. The order of magnitude of the error is ascertained for this and two other approximate methods. Higher-order terms in the approximation are developed.

INTRODUCTION

The usefulness of thermogravimetry (TG) for studying pyrolysis of solids prompted investigations of approximate graphical methods that are suitable for accurate and efficient data reduction[1–3]. For a single-reaction, first-order, Arrhenius process in a sample whose temperature is programmed to increase linearly with time, a detailed numerical comparison[3] illustrated the relative accuracy of three such methods, but the underlying reasons for this relative ranking remained unclear.

As are many other processes in reacting systems, TG tests are characterized by large values of the nondimensional activation energy, z, which is defined by $z = E/RT$, where E is the activation energy, R is the universal gas constant, and T is a representative temperature attained by the system during the process. Typical values of this parameter for TG range from 25 to 100; they rarely fall appreciably below 10. Recent developments in asymptotic analysis[4], when applied to chemically reacting systems[5,6], enable one to extract asymptotic expansions that are valid in the limit of large nondimensional activation energies. It is the purpose of the present communication to develop such an asymptotic expansion for the TG curve of weight loss as a function of temperature. The asymptotic expansion will be employed as a basis for comparing the three approximate methods identified previously. In addition, higher-order terms will be given.

FORMULATION

Although the general approach can be applied for kinetics of greater complexity, attention will be restricted to the weight changes in a single-reaction Arrhenius process in a system whose temperature is increasing linearly with time, t, at a rate $\mathrm{d}T/\mathrm{d}t = u$.

For a pure solid substance pyrolized in an inert medium via a reaction in which at least some of the pyrolysis products are volatile, W_t, the weight at a given time, is related to the fraction, y, of the number of initial molecules not yet decomposed by the equation

$$y = (W_t - W_\infty)/(W_0 - W_\infty). \qquad (1)$$

For clarity, the reaction will be assumed to be of first order; in the appendix the results are extended to reactions of order $n \neq 1$. Combining the above definition and restrictions, one obtains

$$\mathrm{d}y/\mathrm{d}t = -Ay\mathrm{e}^{-z} \qquad (2)$$

or

$$\mathrm{d}y/\mathrm{d}T = -(Ay/u)\mathrm{e}^{-z} \qquad (3)$$

where A is the Arrhenius pre-exponential constant.

Van Krevelen *et al.*[1] observed that most of the reaction occurs over a relatively narrow range of temperatures in the vicinity of T_m, the temperature at which the reaction rate is maximum. The maximum rate is defined by equating to zero the time derivative of eqn (2), *viz.*,

$$A\mathrm{e}^{-z}\,\mathrm{d}y/\mathrm{d}t - Ay\mathrm{e}^{-z}\,\mathrm{d}z/\mathrm{d}t = 0 \qquad (4)$$

which, in view of eqn (3) and the definitions of u and z, yields

$$z_\mathrm{m} = \frac{E}{RT_\mathrm{m}} = \ln\left(\frac{ART_\mathrm{m}^2}{uE}\right) \qquad (5)$$

as an exact although implicit expression for T_m. TG is a useful technique only if A is very large when E is large; the value of A must be such that eqn (5) yields reasonable values of T_m for reasonable values of u.

PREVIOUS APPROXIMATIONS

The previous approximations to $y(T)$ have been developed by making different kinds of expansions of T about T_m. If additive constants of order z_m^{-1} are neglected, then that of van Krevelen *et al.*[1] yields

$$\ln[\ln(1/y)] = (z_\mathrm{m} + 1)\ln(z_\mathrm{m}/z) \qquad (6)$$

while the first alternative of Horowitz and Metzger[2] gives

$$\ln[\ln(1/y)] = z_m[(z_m/z)-1] \tag{7}$$

and their second

$$\ln[\ln(1/y)] = -z+z_m. \tag{8}$$

For all three of these equations, $\ln[\ln(1/y)] = 0$ at $T = T_m$.

Since $z_m/z = T/T_m$, eqns (6), (7), and (8) predict straight lines when $\ln[\ln(1/y)]$ is plotted versus $\ln T$, T, and $-1/T$, respectively. From these lines E may be computed as

$$\left\{\frac{\Delta\{\ln[\ln(1/y)]\}}{\Delta(\ln T)} - 1\right\} RT_m \text{ for eqn (6),}$$

$$\left\{\frac{\Delta\{\ln[\ln(1/y)]\}}{\Delta T}\right\} RT_m^2 \text{ for eqn (7), and}$$

$$\left\{\frac{\Delta\{\ln[\ln(1/y)]\}}{\Delta(-1/T)}\right\} R \text{ for eqn (8).}$$

To illustrate the closeness of these approximations, Fig. 1 shows the exact solution plotted on each of the three graphs suggested by eqns (6), (7) and (8) over

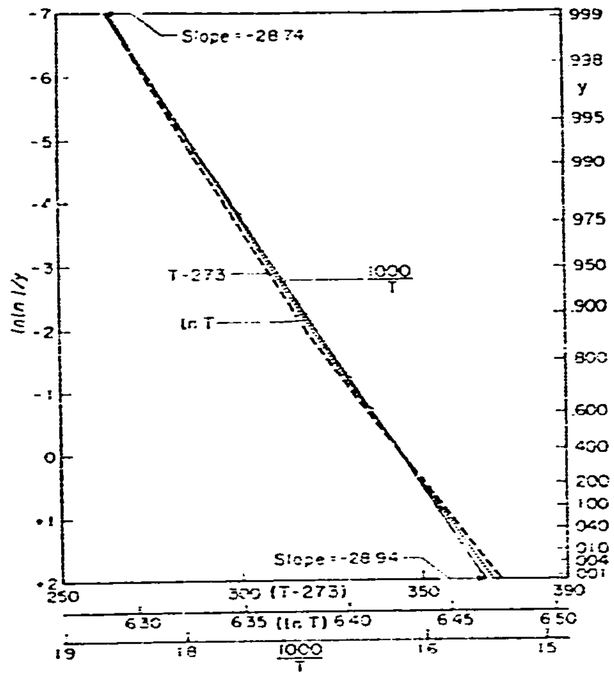

Fig. 1. Deviations from the linearity predictions of eqns (6), (7) and (8) for a heating rate of 5 °C/min and a simple first-order reaction with $A = 1.15 \times 10^{19}$ min^{-1} and $E = 55$ kcal/mole (from ref. 3).

the range $0.999 > y > 0.001$ for a numerical example[3] in which $A = 1.15 \times 10^{19}$ min^{-1}, $E = 55$ kcal/mole, and $u = 5$°C/min. The error in the derived activation energy depends upon how the slopes are determined. If the assumption of linearity over the entire curve is maintained and the slopes determined using the two end points in Fig. 1, then the activation energy is overestimated by about 4 kcal/mole using eqn (6) and by nearly 8 kcal/mole using eqn (7), but these errors decrease appreciably if the slope is obtained in the vicinity of T_m.

With eqn (8) the deviation from linearity in Fig. 1 is imperceptible. Regardless of where the slope is taken along the curve, the value obtained for the activation energy is too large by 2.3 ± 0.2 kcal/mole. The slopes shown at the two ends of the curve were obtained from the tables of Vallet[7]. A constant correction factor, derived from Vallet's tables, gives an activation energy in error by only 0.2 kcal/mole even at the extreme slopes[3].

ASYMPTOTIC ANALYSIS

Since $y = 1$ and $T = T_0$ at $t = 0$, integration of eqn (3) from T_0 to T produces

$$\ln\left(\frac{1}{y}\right) = \frac{A}{u}\int_{T_0}^{T} e^{-z'}\,\mathrm{d}T' \tag{9}$$

where dummy variables of integration have been identified by primes. Strictly speaking, $t = 0$ at the start of a TG run, and T_0 is the ambient temperature (at which a freshly prepared sample of weight W_0 may decompose at a significant rate); the following equations cover this general case. However, in the typical TG experiment the ambient reaction rate is immeasurably slow and the first detectable weight change occurs when a temperature T_1 appreciably above T_0 is reached. For such experiments T_0 arbitrarily may be taken as any temperature below T_1—even, if desired, a temperature below ambient—and the temperature-range restrictions specified below are of no concern.

If, then, $x = z' - z$ is introduced as the variable of integration, and if eqn (5) is used to eliminate A/u, then eqn (9) becomes

$$\ln(1/y) = [\exp(z_m - z)](z_m/z)^2 I(z,s) \tag{10}$$

where

$$s = (T - T_0)/T_0 \tag{11}$$

and

$$I(z,s) = \int_0^{sz}\left(1 + \frac{x}{z}\right)^{-2} e^{-x}\,\mathrm{d}x. \tag{12}$$

Equation (10) is exact since no approximations have been introduced.

The factor e^{-x} makes the integrand in eqn (12) small when x is large. For large values of z, one can therefore generate an asymptotic expansion of I by first introducing the expansion

$$\left(1+\frac{x}{z}\right)^{-2} = \sum_{n=0}^{\infty} (n+1)\left(-\frac{x}{z}\right)^{n} \tag{13}$$

then integrating term by term. There results

$$I(z, s) \sim \sum_{n=0}^{\infty} (n+1)(-z)^{-n} \int_{0}^{sz} x^{n} e^{-x} \, dx. \tag{14}$$

The integrals remaining in eqn (14) are incomplete gamma functions, and they must be retained as such if the expansion is to be uniform in s for $0 \leq s \leq \infty$. However, if sz is large, which will be true for large values of z unless s is of order $1/z$ or smaller, then asymptotic expansions of the integrals in eqn (14) can be used to simplify the asymptotic expansion of I. Thus

$$\begin{aligned}
\int_{0}^{sz} x^{n} e^{-x} \, dx &= \int_{0}^{\infty} x^{n} e^{-x} \, dx - \int_{sz}^{\infty} x^{n} e^{-x} \, dx \\
&= n! - e^{-sz} \int_{0}^{\infty} (sz+v)^{n} e^{-v} \, dv \\
&= n! - e^{-sz} (sz)^{n} \sum_{m=0}^{n} m! \binom{n}{m} (sz)^{-m}.
\end{aligned} \tag{15}$$

Equation (14) becomes

$$I(z, s) \sim \sum_{n=0}^{\infty} (n+1)!(-z)^{-n} - e^{-sz} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (n+1)\, m! \binom{n}{m} (-s)^{n} (sz)^{-m}. \tag{16}$$

This expansion is valid for z approaching infinity in such a way that sz approaches infinity.

The restriction on sz is satisfied approximately for $sz > 1$, which defines a range of temperatures, very near the initial temperature, for which eqn (16) is not valid. For large values of z, this restricted range is quite small and generally of no interest. Thus for typical values of z and for T_0 about 300 K, the excluded range is roughly 10°C above ambient. In the usual TG experiment only negligible reaction will have occurred, *i.e.*, the value of y will still be exceedingly close to unity.

If s remains of order unity as z approaches infinity then, because of the factor e^{-sz}, the double sum in eqn (16) is exponentially small compared with each term in the first sum. In this case, the correct asymptotic expansion is obtained by deleting the double sum. There are limits, *e.g.*, s proportional to $(1/z)\ln z$, in which low-order terms in the double sum are larger than high-order terms in the first sum. Nevertheless, in typical TG experiments, the double sum, which describes the dependence of the thermogram on the initial temperature, will be negligibly small. In these cases, substitution of the approximate expansion obtained from eqn (16) into the expression appearing in eqn (10) produces, after the logarithm of the result is taken, the asymptotic expansion

$$\ln\left[\ln\left(1/y\right)\right] \sim -z+z_{\mathrm{m}}+2\ln\left(z_{\mathrm{m}}/z\right)+\ln\left[\sum_{n=0}^{\infty}(n+1)!(-z)^{-n}\right] \tag{17}$$

which is valid for the limit of z approaching infinity.

Through terms of order $1/z$, eqn (17) is

$$\ln[\ln(1/y)] = -z+z_{\mathrm{m}}+2\ln(z_{\mathrm{m}}/z)-2/z+O(z^{-2})+O(e^{-sz}) \tag{18}$$

where the order of the terms discarded by neglecting the double sum also has been indicated explicitly.

COMPARISONS

It should be clear that the preceding development nowhere involved the assumption that $(T-T_{\mathrm{m}})/T_{\mathrm{m}}$ is small. In this respect, it differs from the previous approximations. The only approximations underlying eqn (18) are represented by the requirements that $1/z$ and e^{-sz} be small. Typically $z = 50$, so that the error stemming from neglect of the term $O(z^{-2})$ in eqn (18) is 0.0004. The error stemming from neglect of the final term in eqn (18) will not exceed this provided that $s>0.16$, which corresponds roughly to a temperature rise of 50°C above ambient.

At the extremes of a typical TG curve, *e.g.*, for the temperature at which $y = 0.999$ in Fig. 1, this error is approximately two orders of magnitude less than that calculated for the best of the previous approximations. If the term $-2/z$ is neglected in eqn (18), then the error using this equation remains one order of magnitude less than that using eqn (8), and the restriction on s reduces approximately to the requirement that the temperature has risen 20°C.

Since the determination of activation energies from TG data utilizes the slope of the approximate curve, minimum departure from linearity, perhaps more than minimum absolute error in $\ln[\ln(1/y)]$, will facilitate accurate reduction of data. The linearity of graphs for eqns (6), (7) and (8) can be tested on the basis of eqn (18). Comparison of eqn (18) with eqns (6), (7) and (8) reveals that of the three previous approximations, only eqn (8) is identical with eqn (18) up to terms of order $\ln(z_{\mathrm{m}}/z)$. Thus, the particular expansion about T_{m} given in eqn (8) fortuitiously agrees with the first term of an asymptotic expansion in the large parameter z. This can explain the high degree of linearity exhibited for eqn (8) in Fig. 1. Differentiation of eqn (18) reveals that the slope corresponding to eqn (8), $d\ln[\ln(1/y)]/dz$, is $-1 \ -2/z+\ldots$, which varies only from -1.037 to -1.044 at the extremities of the figure. On the other hand, differentiation of eqn (18) with respect to $\ln z$ or $1/z$ exhibits a much greater variation in slope.

To derive eqn (6) or (7) from eqn (18) necessitates introducing expansions about $T = T_m$. Two such expansions are

$$\frac{1}{T} = \frac{1}{T_m}\left[1 - \left(\frac{T-T_m}{T_m}\right) + \ldots\right] \tag{19}$$

and

$$\frac{1}{T} = \frac{1}{T_m}\left[1 - \ln\left(\frac{T}{T_m}\right) + \ldots\right]. \tag{20}$$

The lowest-order version of eqn (18), *i.e.*, eqn (8), is converted to eqn (7) by introducing eqn (19) and to

$$\ln[\ln(1/y)] = z_m \ln(z_m/z) \tag{21}$$

by introducing eqn (20). If the logarithmic term is retained in eqn (18), then the expansion about T_m given in eqn (20) produces

$$\ln[\ln(1/y)] = (z_m + 2)\ln(z_m/z). \tag{22}$$

For large z neither eqn (21) nor eqn (22) differs significantly from eqn (6).

In view of the established high degree of linearity for eqn (8), the observation (Fig. 1) that eqn (6) is more nearly linear than eqn (7) can be explained from the fact that the lowest-order approximation to eqn (6), *viz.*, eqn (21), agrees better with eqn (8) than does eqn (7). This can be seen by making two-term expansions of eqns (7), (8) and (21) about $T = T_m$. Expressed in terms of $T - T_m$, the expansion is simply

$$z_m\left(\frac{T-T_m}{T_m}\right) \text{ for eqn (7),}$$

$$z_m\left[\left(\frac{T-T_m}{T_m}\right) - \left(\frac{T-T_m}{T_m}\right)^2 + \ldots\right] \text{ for eqn (8), and}$$

$$z_m\left[\left(\frac{T-T_m}{T_m}\right) - \frac{1}{2}\left(\frac{T-T_m}{T_m}\right)^2 + \ldots\right] \text{ for eqn (21).}$$

Clearly, the last of these is about twice as good as an approximation to the second, than is the first. Stated differently, the relevant observation is that for the expansion of $1/T$ about $T = T_m$, the function $\ln(T/T_m)$ looks more like the exact function, *viz.* $(T - T_m)/T$, than does $(T - T_m)/T_m$. But of course, formally the error is of the same order for eqns (6), (7), (21) and (22), *viz.*, of order $z_m[(T - T_m)/T_m]^2$.

These relationships further emphasize that an expansion about T_m is not strictly justified from an asymptotic viewpoint, that contributions occur from higher-order terms in such an expansion, and that the reaction does proceed at temperatures differing appreciably from T_m. Nevertheless, in some sense *most* of the reaction does occur near T_m when the activation energy is large. The sense in which this is true can be seen from eqn (18) in lowest order, *i.e.*, eqn (8). In the derivation of eqn (18), explicit restrictions were imposed on T but not on the range of y. Implied restrictions on y are exceedingly lenient, especially in the range of small y. On the other hand, suppose that one is interested only in the intermediate range of y over which the bulk of the reaction occurs, *i.e.*, the range defined by the sensitivity of the instrumentation. This range can be specified by requiring $-a < \ln[\ln(1/y)] < b$, where a and b are fixed positive numbers.

It is clear from eqn (8) that as z_m approaches infinity, the corresponding temperature range, *i.e.*, $T_m(1+a/z_m)^{-1} < T < T_m(1-b/z_m)^{-1}$, narrows about T_m. If a/z_m and b/z_m are small compared with unity, then the relevant range of T becomes $-a/z_m < (T-T_m)/T_m < b/z_m$, which justifies the expansions underlying eqns (6) and (7). As z_m approaches infinity, all of the expansions become equivalent and correct for $-a < \ln[\ln(1/y)] < b$. However, usually values of a and b that exceed unity are of interest[3], and in such cases the restrictions $a/z_m \ll 1$ and $b/z_m \ll 1$, needed to justify the expansion about T_m, are somewhat more stringent than the restriction $1/z \ll 1$, needed to justify the asymptotic expansion.

GRAPHICAL METHOD OF IMPROVED ACCURACY

Differentiation of eqn (18) provides a simple means of improving the accuracy in determining E from the plot of eqn (8). Through terms of order $\ln z$ in eqn (18),

$$\frac{d\{\ln[\ln(1/y)]\}}{d(1/T)} = -\frac{E}{R}\left(1+\frac{2}{z}\right). \tag{23}$$

For $z = 50$, then, the assumption of a constant slope with value E/R is in error by 4%. For the example in Fig. 1 this corresponds to an error of roughly 2 kcal/mole in E. However, in the usual case (see Fig. 1), the temperatures of interest fall within a narrow range about some intermediate temperature, T_i. If this range is within 10% of T_i, the assumption that $T = T_i$ in the last term of eqn (23) leads to the following as an estimate of E that is better by an order of magnitude than that obtained directly from eqn (8):

$$E = \left\{\frac{\Delta\{\ln[\ln(1/y)]\}}{\Delta(-1/T)}\right\} R - 2RT_i. \tag{24}$$

For example in Fig. 1, use of eqn (24) is equivalent to multiplying the slope for eqn (8) by 0.96 [as in eqn (19) of ref. 3] and gives a value of E in error by no more than 0.2 kcal/mole. Within this accuracy T_i may be taken as any temperature between the extremes of the curve. The value $T_i = T_m$ may be used, but if, instead, the midpoint temperature (i.e., the temperature at which $y = 0.92$) is chosen, the error in E is reduced to about 0.05 kcal/mole.

Should such improvement be warranted, a better means of obtaining the more accurate value of E graphically [by a reduction of the curvature in the line for eqn (8)] is also provided by eqn (18). Instead of plotting $\ln[\ln(1/y)]$ versus $(1/T)$, one may plot $\ln[\ln(1/y)] - 2\ln(T/T_m)$ versus $1/T$. Alternatively, one may simply plot $\ln[\ln(1/y)] - 2\ln T$ and not bother to observe T_m. According to eqn (18), up to terms of order $1/z$ or e^{-sz}, whichever is larger, the graph in either case will be a straight line with a slope of $-E/R$.

APPENDIX

For a reaction of order n, eqn (1) is

$$dy/dt = -ky^n \tag{A1}$$

and eqn (5) becomes

$$\frac{E}{RT_m} = \ln\left(\frac{nART_m^2\, y_m^{\,n-1}}{uE}\right). \tag{A2}$$

The analog of eqn (9) is

$$\frac{1}{y^{n-1}} - 1 = (n-1)\left(\frac{A}{u}\right)\int_{T_0}^{T} e^{-z'}\, dT'. \tag{A3}$$

As expected, eqn (A3) demonstrates that y approaches zero only as T approaches infinity for $n > 1$, but y reaches zero at a finite value of T for $n < 1$.

It is easily found that what corresponds to eqn (10) is

$$\frac{1}{y^{n-1}} - 1 = [\exp(z_m - z)]\left(\frac{z_m}{z}\right)^2\left(\frac{n-1}{ny_m^{\,n-1}}\right) I(z, s), \tag{A4}$$

where I again is given by eqn (12). It thus becomes clear that the generalization of eqn (18) is

$$\ln\left(\frac{1}{y^{n-1}} - 1\right) = -z + z_m + \ln\left(\frac{n-1}{ny_m^{\,n-1}}\right) + 2\ln\left(\frac{z_m}{z}\right) - \frac{2}{z} + O(z^{-2}) + O(e^{-sz}). \tag{A5}$$

A plot of $\ln[y^{-(n-1)} - 1] - 2\ln T$ versus $1/T$ provides a quite stringent linearity test for an nth-order reaction and yields the activation energy from the slope $-E/R$.

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