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A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data*

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Synopsis

Thermogravimetric Analysis (TGA) is finding increasing utility in investigations of the pyrolysis and combustion behavior of materials. Although a theoretical treatment of the TGA behavior of an idealized reaction is relatively straight-forward, major complications can be introduced when the reactions are complex, e.g., in the pyrolysis of cellulose, and when experimental imperfections arise. Consequently, a fairly large number of analytical methods have been proposed for obtaining kinetic parameters from TGA curves. Among the proposed methods are several graphical procedures, mostly involving relatively inaccurate tehniques, such as obtaining slopes on a rapidly changing curve. Included among the proposed procedures is one which permits a linear plot of TGA data. The sensitivity with which such a plot can be used to identify and correct for a variety of experimental complications seems to have escaped even the proponents of the techniques. This paper provides an illustration of the use of this graphical procedure in a hypothetical first-order pyrolysis typical of those occurring in the TGA behavior of cellulose.

INTRODUCTION

Thermogravimetric analysis (TGA) is finding increasing utility in investigations of the pyrolysis and combustion behavior of solids.[1–3] If, for example, a piece of cellulose is heated in an inert atmosphere at a linearly programmed rate, a record of its weight as a function of time produces a curve such as that shown in Figure 1.[4] Such data can provide clues about the number and sequence of reactions which occur in a pyrolysis process, and about such kinetic parameters as the order and activation energy of these reactions.

Also shown in Figure 1 are three curves of single-reaction, first-order processes, normalized to give approximate fits to the cellulose pyrolysis curve. It appears obvious that the cellulose decomposition cannot be represented by a single first-order reaction, but nevertheless, the theoretical curves represent a weight-temperature behavior which is roughly comparable to that of cellulose during a significant portion of its weight loss.

Differentiating Curve B in Figure 1 gives the result shown in Figure 2. As may be seen, the decomposition occurs at a very slow rate until a critical

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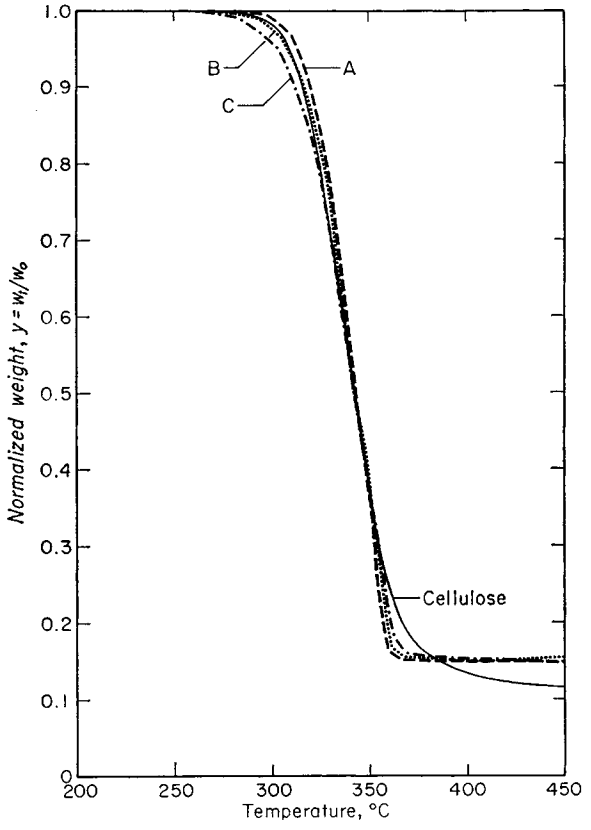

Fig. 1. Thermogram of cellulose pyrolysis (from Ref. 4). Also shown are three theoretical curves computed for first-order reactions with 15% char, peak reaction rate at 344°C and activation energy: curve A = 65000 cal/mole, curve B = 55000 cal/mole, and curve C = 45000 cal/mole.

temperature region is reached. Then the pyrolysis rate increases very rapidly to a maximum, after which, as the sample disappears, the rate drops even more rapidly. Such behavior is characteristic of a large number of decomposition processes, including many polymer pyrolyses, and a large number of methods have been proposed for obtaining the kinetic parameters of such reactions from the recorded thermogram or its derivative.[5–7] The proposed methods differ widely in their complexity and in the accuracy of the results which may be obtained.

As early as 1951, Van Krevelen *et al.*[8] proposed an approximate transformation of the thermogram to give a linear plot from which the activation energy and pre-exponential factor could be easily extracted. In 1963, Horowitz and Metzger[9,10] introduced this procedure with variants, indicating that its utility had apparently not been appreciated. Horowitz and Metzger demonstrated the usefulness of the method in analyzing the pyrolysis behavior of a number of materials over the range of 3–90% decom-

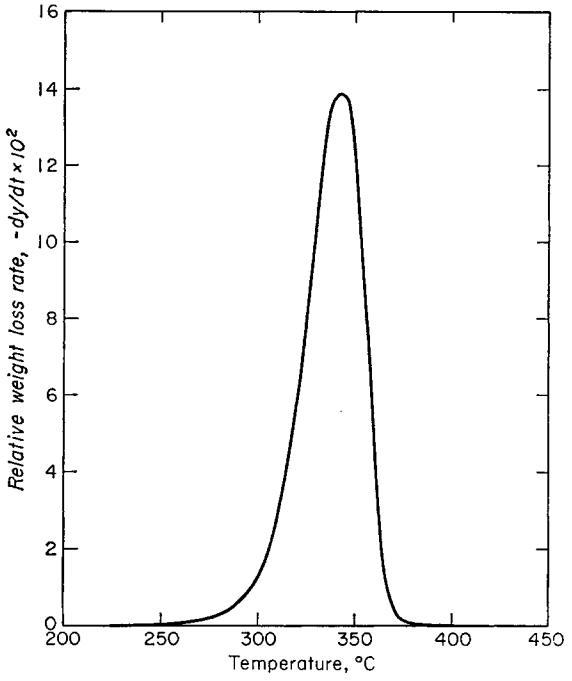

Fig. 2. Reaction rate vs. temperature for $E = 55000$ cal/mole.

position. However, they, too, seem to have overlooked the extreme sensitivity of the method and its utility in obtaining information in the region outside this range of maximum pyrolysis reaction.

It is the purpose of the present paper to demonstrate, via theoretical curves such as those in Figure 1, the utility of this analytical procedure in detecting small experimental deviations which may be introduced by small amounts of impurities in the sample or by irregularities in the experimental apparatus. A subsequent paper[11] will provide confirmation of the method's usefulness in resolving "real" experimental results, *viz.*, those obtained with ammonia-swelled cellulose.

Theory

Suppose that a pure solid substance heated in a vacuum undergoes pyrolysis via a reaction in which at least some of the pyrolysis products are volatile. The progress of the reaction can be determined by continuous weighing of the sample. W_t, the weight at any time, t, is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation

$$y = N/N_0 = (W_t - W_\infty)/(W_0 - W_\infty) \tag{1}$$

If the pyrolysis is carried out isothermally, the reaction rate is given by

$$dy/dt = -ky^n \tag{2}$$

in which n is the reaction order. If the rate constant, k, changes with absolute temperature according to the Arrhenius equation:

$$k = Ae^{-E/RT} \tag{3}$$

and if, instead of operating isothermally, the temperature, T, is a linear function of t, i.e.,

$$T = T_0 + ut, \tag{4}$$

eqs. (2), (3), and (4) may be combined to give

$$dy/y^n = -(A/u)e^{-E/RT}dT \tag{5}$$

The TGA curve for such a reaction represents this last equation integrated from a temperature T_0 at which $y = 1$. Thus,

$$\int_y^1 dy/y^n = A/u \int_{T_0}^{T} e^{-E/RT}\, dT. \tag{6}$$

Since a large number of pyrolysis processes can be represented as first-order reactions, we shall consider mainly such reactions for the remainder of the present paper. Therefore,

$$\int_y^1 dy/y^n = \int_y^1 dy/y = -\ln y = \ln(1/y). \tag{7}$$

Of course, for orders other than unity the integration of the left-hand part of eq. (6) is equally straight-forward. Conversely, the integration of the right-hand part of eq. (6) is anything but simple. However, Vallet, in a tri-lingual monograph published in 1961,[12] makes the substitution.

$$z = E/RT \tag{8}$$

and reduces the integration to that for the expression

$$J(z) = \int_z^\infty z^{-2}e^{-z}dz = z^{-2}e^{-z}S(z). \tag{9}$$

Vallet tabulates the rapidly changing $J(z)$ and the slowly varying $S(z)$ for values of z from 1 to 200, thus covering the range of interest for most problems. This tabulation has been used in computing the theoretical values of y throughout the present paper. In particular, for a simple, first-order reaction, y has been computed from the equation

$$\ln y = -(AE/uR)J(z) \tag{10}$$

Approximations

Van Krevelen et al.,[8] noting that almost the entire measurable reaction usually occurs within $\pm 10\%$ of T_m, the temperature of maximum reaction velocity, applied the following approximations to the right-hand part of eq. (6):

$$e^{-E/RT} = (e^{-T_m/T})^{E/RT_m} \simeq [(T/T_m)e^{-1}]^{E/RT_m} \tag{11}$$

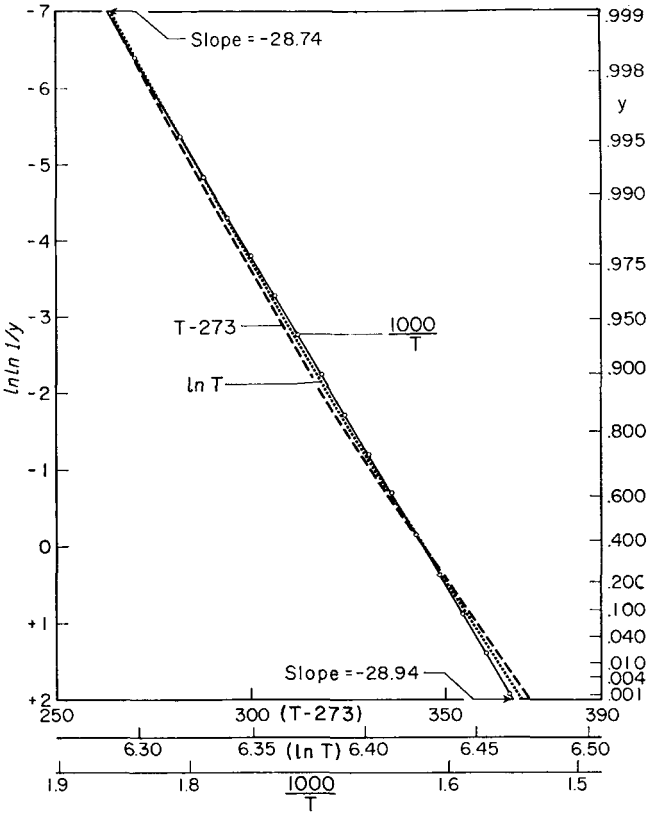

Fig. 3. Plot of ln ln $(1/y)$ vs. T, ln T, and $1000/T$. The extreme slopes for the $1000/T$ curve were computed using eq. (18) and Table I of Ref. 12.

By integrating and taking logs of both sides of eq. (6), then, one obtains

$$\ln \ln(1/y) = (E/RT_m + 1) \ln T + \text{const.} \tag{12}$$

Thus, a plot of ln $\ln(1/y)$ vs. ln T yields a straight line whose slope is related to the energy of activation.

Horowitz and Metzger[10]* introduced two alternate approximations. Since

$$T_m/T = (T_m/T + T/T_m) - T/T_m = (T_m^2 + T^2)/TT_m - T/T_m, \tag{13}$$

the assumption that $T_m^2 + T^2 \simeq 2T_mT$ means that

$$e^{-E/RT} = e^{(-E/RT_m)(T_m/T)} \simeq e^{-(E/RT_m)(2-T/T_m)}. \tag{14}$$

On integration, then, this assumption yields

$$\ln \ln(1/y) = (E/RT_m^2)T + \text{const.} \tag{15}$$

* The reader is cautioned to beware of several typographical errors in the equations of this reference.

which provides a simpler abscissa than does eq. (12). On the other hand, the assumption that

$$e^{-E/RT} \simeq (T_m/T)^2 e^{-E/RT} \tag{16}$$

leads to

$$\ln \ln(1/y) = -(E/R)(1/T) + \text{const.} \tag{17}$$

which is, surprisingly perhaps, the most accurate of the three integrated equations.

The degree to which eqs. (12), (15), and (17) yield a straight-line relationship is illustrated in Figure 3, which was computed for curve B of Figure 1, viz., for the values: $A = 1.1507 \times 10^{19}$/min; $E = 55000$ cal/mole; $R = 1.987$ cal/mole°C; $u = 5$°C/min.

For eq. (17), only the computed points are shown and the line through these points is drawn with a straight edge. As can be seen, the plot of $\ln \ln(1/y)$ vs. $1/T$ gives an excellent approximation to a straight line over the range $0.999 > y > 0.001$. Although the deviation from linearity cannot be detected in the figure, Vallet's tabulations provide a means of estimating this deviation. From Vallet's definitions of J, S, and z, it may be shown that:

$$d[\ln \ln(1/y)]/d(1/T) = [-1/S(z)][dz/d(1/T)] = [-1/S(z)][E/R] \tag{18}$$

Over the range covered in Figure 3, $S(z)$ varies from 0.9633 to 0.9564. Thus, over this entire reaction range, the assumption that

$$E = 0.960R\Delta[\ln \ln(1/y)]/\Delta(1/T) \tag{19}$$

is in error by less than 0.2 kcal/mole.

It should be noted that while the example above represents a fairly narrow decomposition peak, the method is only slightly less accurate with much broader decomposition temperature ranges. Thus, even with activation energy as low as 10 kcal/mole and T_m as before (i.e., with preexponential factor $A = 2.8 \times 10^2$), the error introduced by the assumption of constant slope over the significant temperature range (80–500°C) is comfortably less than 1 kcal/mole. With this low E and larger values of A, the error decreases. In fact, $S(z)$ changes so slowly that $0.8 < S(z) < 1$ covers all values of $z > 7$ (i.e., $E/T > 14$).

Effect of Sample and Instrumental Errors

If a sample decomposes via more than one reaction and the sequence of reactions are sufficiently displaced in temperature, the sequence shows up quite readily in a direct plot of the TGA curve. On the other hand, if two or more reactions occur within the same temperature range, it is frequently well nigh impossible to separate the reactions, or even recognize that more than one reaction is occurring, by a direct examination of the thermogram. Thus, Figure 4a compares the thermogram which would be obtained if a particular sample reacted entirely as in curve B of Figure 1 with that for a sample, half of which reacted as in curve A ($A = 4.6975 \times 10^{22}$/min,

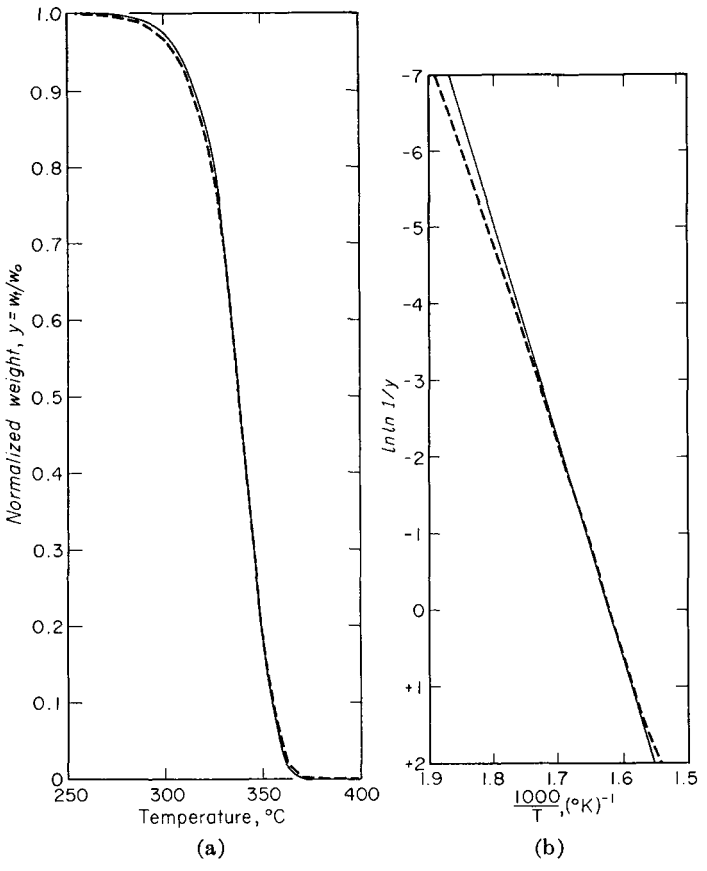

Fig. 4. Comparison of thermogram for $E = 55000$ cal/mole (solid line) with equal proportions reacting at $E = 45000$ and 65000 cal/mole: (a) Plot of normalized weight vs. temperature; (*b*) Plot of $\ln \ln(1/y)$ vs. $1000/T$.

$E = 65000$ cal/mole) and the other half as in curve C ($A = 2.7463 \times 10^{15}$/min, $E = 45000$ cal/mole). As may be seen, the two curves are almost identical. On the other hand, the same data are plotted in Figure 4b, this time as $\ln \ln(1/y)$ vs. $1/T$. Here the distinction between the two situations is quite unmistakable, as may be seen particularly well by placing a straightedge tangent to the beginning or end portions of the dashed curve.

The extreme sensitivity of the linear plot shows up best, however, when one looks at the effect of small instrumental errors, e.g., zero drift of the balance as the result of thermomolecular flow, or of small amounts of extraneous material, e.g., water, which can give a misleading value of initial sample weight. Suppose, for example, the sample contained 1% water at the start of the experiment and this water evaporated prior to the onset of the pyrolysis reaction. Such a 1% correction in W_0 would just barely show up in a plot of y vs. T. On the other hand, it would produce the rather striking result given by curve A in Figure 5. If this water diffused

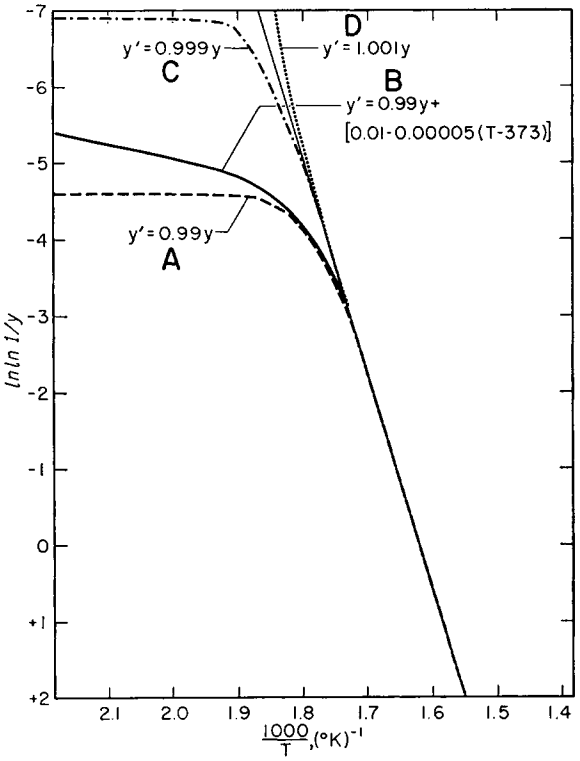

Fig. 5. Effect on ln ln$(1/y)$ plot of small errors in W_0.

from the sample more slowly, say, linearly with time as the sample was heated from 100° to 300°, the ln ln plot would give a result like that in curve B. Even if W_0 was in error by as little as ± 0.001, the result would show up quite clearly on the ln ln plot, as in curves C and D.

Suppose, instead, that the initial sample was pure but the gaseous pyrolysis products did not diffuse from the reaction zone sufficiently rapidly to avoid secondary reactions leading to a solid residue or char. Figure 6 illustrates the sensitivity of the linear plot in detecting such a char. Suppose that the output of the TGA furnace is not sufficient to maintain the linear heating rate at the upper end of the temperature range. If the heating rate dropped linearly from say, 5°/min at 250°C to 4.5°/min at 375°C, the ln ln plot would deviate from linearity as shown in Figure 7.

Suppose the pyrolysis reaction were highly endothermic. Then, during the rapid pyrolysis stages, the sample temperature would be cooler than the recorded furnace temperature. Suppose the maximum temperature difference were 2° and the difference were always proportional to the pyrolysis rate as given in Figure 2. As seen in Figure 8, the result of such an effect would be quite readily noticeable.

Finally, suppose the assumption that the reaction is first order is in error. Figure 9 shows the deviations from linearity which would be observed for

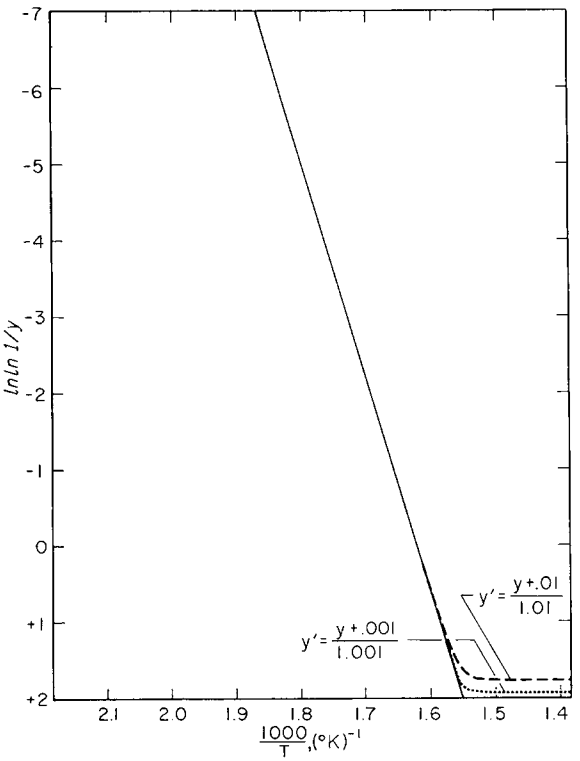

Fig. 6. Effect on ln ln $(1/y)$ plot of small errors in W_∞.

reactions with identical activation energy and pre-exponential factor, but with order 0, 0.5, 0.9, 1.1 and 2. As would be expected, the early portion of the plot is essentially order-independent, but the terminal portion is highly sensitive to reaction order.

DISCUSSION

As has been shown, the plot of ln $\ln(1/y)$ vs. $1/T$ provides an extremely sensitive method of detecting small deviations in an otherwise simple, unique pyrolysis reaction. Although the reasons for deviations from linearity are not always unambiguous, the extreme sensitivity of the plot to minute changes means that the ability to obtain a linear relationship over the entire range is highly indicative of a single, first-order Arrhenius reaction. In fact, this treatment of the data may actually permit a more accurate estimate of such parameters as the initial sample weight than can be obtained by direct experiment. Such sensitivity is particularly useful in separating component reactions in a more complicated pyrolysis process. Thus, for each component a small error in estimating the fraction of the weight change due to that particular component shows up quite strikingly

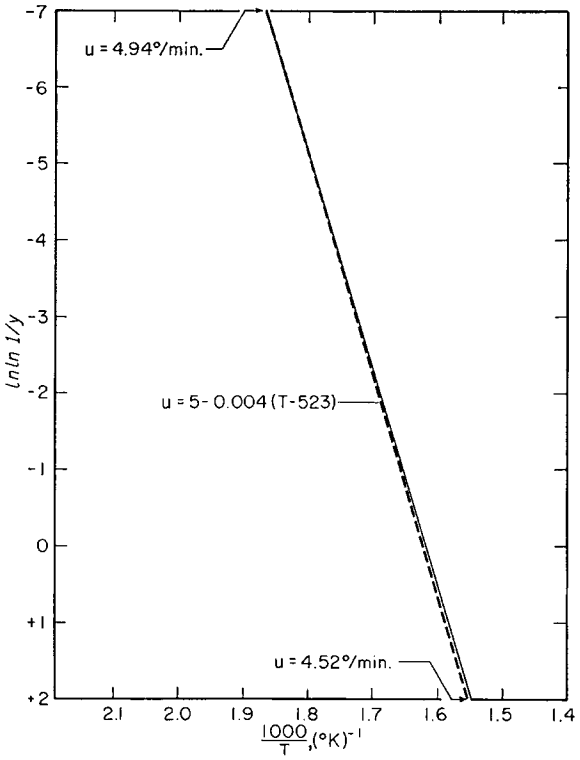

Fig. 7. Effect of nonlinearity in rate of temperature increase.

in its ln ln plot. Subsequent iterations to eliminate such effects can thus lead to a very accurate estimate of the fractional contribution.

Only considerably more experience can establish the practical utility of a linearizing procedure such as described here in sorting out and identifying the various deviations which are always found in experimental data. Where several nonrandom experimental inaccuracies of the type discussed each provide major deviations, a simple decomposition scheme may be quite effectively masked. Nevertheless, results with a limited number of systems have been quite encouraging. As a minimum, the procedure has proved useful in distinguishing between random and systematic deviations in thermograms.

Appendix

When this paper was submitted to the journal, one of the referees kindly took the trouble to note that the experimental cellulose curve in Figure 1 closely resembled that for a second-order reaction with activation energy of 60 kcal/mole. As shown in Figure 10a, the parameters assumed by this referee give an excellent fit to the central three-fourths of the experimental curve and what appears to be a fairly reasonable fit over the rest of the

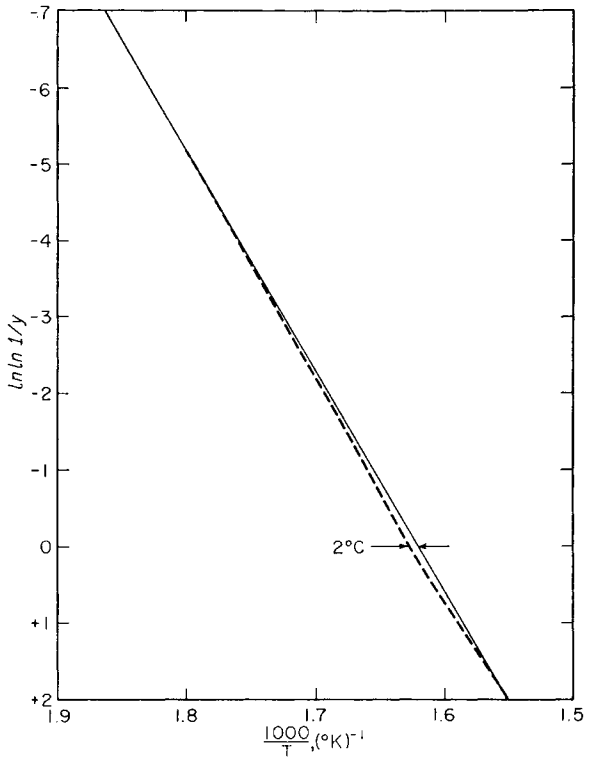

Fig. 8. Effect of sample cooling by endothermic reaction.

range. Nevertheless, the assumption of a single, second-order reaction contradicts a wealth of other information known about cellulose, e.g., its isothermal behavior, the changes in its TGA curve as heating rate is changed and its behavior as "fire-retardant" catalysts are added. The most obvious illustration of this is that the material should give the same yield of char regardless of heating rate if it followed a single reaction; but instead, the residue varies by about a factor of 4 as heating rate is changed. Thus, if the TGA curve can be represented by a single, second-order reaction, the technique leaves something to be desired if it is to be used to correctly interpret cellulose pyrolysis behavior.

This example provides an excellent illustration of the motivation for the present publication. TGA curves, which offer an extremely effective short cut to the accumulation of considerable kinetic data, must be treated with great caution if they are not to add more confusion than enlightenment. In particular, the "slight" deviations at both ends of the thermogram can be most significant, and it is important to be able to detect them. In the above example, if cellulose did pyrolyze via a second-order process, a plot of $\ln[(1 - y)/y]$ vs. $1/T$ should give a straight line. As may be seen in Figure 10b, the referee's theoretical curve when replotted in this way

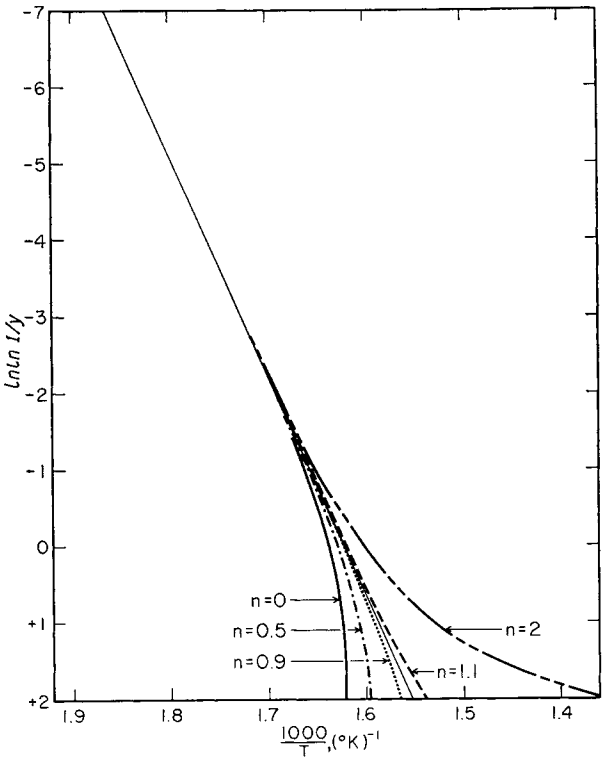

Fig. 9. Deviations from linearity of an assumed first-order plot if the actual reaction order is 0, 0.5, 0.9, 1.1 or 2.

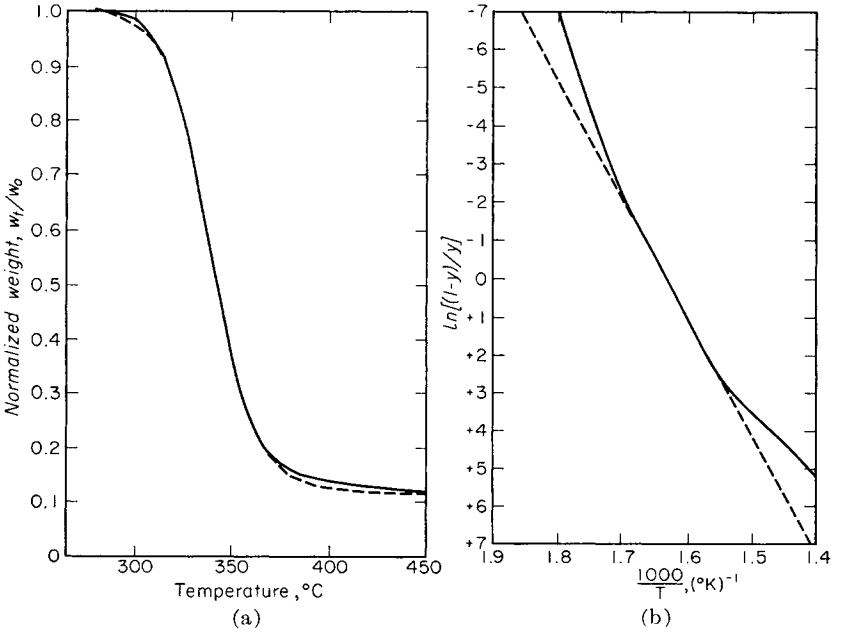

Fig. 10. Comparison of experimental cellulose thermogram (solid line from Fig. 1) with theoretical curve computed for a second-order reaction, assuming $W_\infty/W_0 = 0.116$, $E = 60$ kcal/mole, and $AE/uR = 6.4759 \times 10^{24}$: (a) Plot of normalized weight temperature; (b) Plot of ln $[(1 - y)/y]$ vs. $1000/T$.

does give a straight line over the entire range, and the experimental curve most decidedly does not.

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