Thermochimica Acta, 5 (1972) 59–69

DETERMINATION OF KINETIC PARAMETERS FOR THE THERMAL DEGRADATION OF POLYMERS BY THE QUASILINEARIZATION TECHNIQUE

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(Received March 22nd, 1972)

ABSTRACT

The thermal degradation of polymers is explored generally by the experimental technique of thermogravimetry (TG). Existing mathematical methods for processing dynamic TG data to obtain kinetic parameters for non-linear models require data obtained at a constant rate of temperature rise and employ one or more graphical techniques, which are time-consuming and lead to some inaccuracy. A recently developed numercial approach to the determination of kinetic parameters which avoids the forementioned problems and provides a rapid, flexible, systematic, and accurate technique is the Bellman–Kalaba method of quasilinearization.

Their general technique is extended and applied to TG data. The method presented utilizes the experimental thermogram(s) directly and selects the kinetic parameters by a least-squares-optimization procedure to best fit the data. The calculations are conveniently carried out on a digital computer. The technique has been applied to data on the thermal degradation of high-temperature polymers including polyphenylene, polyimide and polyquinoxaline.

INTRODUCTION

In an attempt to quantitatively describe the kinetics of thermal decomposition of polymeric materials, a number of laboratory techniques have been employed with some success. Of these, thermogravimetry (TG) probably has been the most widely used experimental tool. The objectives of TG experimentation are the generation of thermograms from which a kinetic model can be formulated which describes the thermal decomposition. TG data are also used in formulating and verifying postulated mechanisms of pyrolysis.

The mathematical analysis of experimental TG data for the purpose of determining the kinetic parameters of a suitable reaction-rate equation has been the subject of many papers and review articles[1–4]. In general, commonly used methods require data obtained from a constant rate of temperature rise, and employ one or more graphical techniques for the determination of kinetic parameters. A recently developed

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numerical method, which avoids these problems and provides a systematic approach to the determination of kinetic constants, is the quasilinearization technique of Bellman and Kalaba[5]. This method utilizes experimental data points directly, and selects kinetic parameters by a least-squares-optimization procedure to best fit the data. The method is iterative and requires an initial assumption of the values of the constants. The lack of guarantee of convergence is the primary difficulty with the approach.

Nevertheless, quasilinearization is a powerful analytical tool which offers three significant advantages over most of the presently employed techniques for analysis of TG data: (*1*) It is not necessary to maintain a constant-rate temperature rise during the experiment. A completely flexible temperature history, including periods of differing rates of temperature rise and even isothermal segments, can be successfully handled. The increased analytical flexibility greatly extends the types of experimentation possible. (*2*) Multiple experimental runs may be combined in a single data analysis if desired. That is, similar experimental thermograms for a given material may be collectively analyzed to yield a single set of optimized kinetic parameters. (*3*) Inaccurate data handling procedures such as graphical data analysis and slope measurements are completely avoided.

DEVELOPMENT OF THE QUASILINEARIZATION METHOD

In applying quasilinearization to TG data, a power law rate function of the following type is usually assumed.

$$-\frac{1}{w_0}\frac{\mathrm{d}w}{\mathrm{d}t} = k\left[\frac{w-w_r}{w_0}\right]^n \tag{1}$$

where w_0 = initial weight of polymer, w_r = final weight of residue after complete degradation, w = instantaneous weight of polymer-residue material during the degradation process, t = time, and n = kinetic order of the degradation reaction.
Eqn. (1) may be written

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = k\,W^n \tag{2}$$

where k = specific rate constant and $W = (w-w_r)/w_0$. The rate constant k is assumed to depend on the absolute temperature according to the Arrhenius law

$$k = A\mathrm{e}^{-E/RT} \tag{3}$$

where A = pre-exponential factor, E = activation energy, R = universal gas constant, and T = absolute temperature.

The problem of determining the kinetic constants A, E, and n in Eqn. (2) is transformed to the estimation of the initial conditions for a system of time-dependent differential equations. This is done by assuming that the constants are functions of time such that the following equations are satisfied.

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -Ae^{-E/RT}\,W^{n},\ W(0) = 1-w_{r}/w_{0}; \tag{4}$$

$$\frac{\mathrm{d}A}{\mathrm{d}t} = 0,\ A(0) = A_{0}; \tag{5}$$

$$\frac{\mathrm{d}E}{\mathrm{d}t} = 0,\ E(0) = E_{0}; \tag{6}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 0,\ n(0) = n_{0}; \tag{7}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \rho,\ T(0) = T_{0}; \tag{8}$$

where ρ is a known function of time. The latter equation is equivalent to having

$$T = \phi(t),\ T(0) = T_{0}.$$

The intent is that all quantities in the equations are functions of time and that the unknowns appear as initial conditions. Eqns. (4)–(7) are linearized by converting them into sequences which, with reasonable initial assumptions will rapidly converge to the best values of the kinetic parameters. Thus, if

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \mathrm{f}(W, A, E, n) \tag{9}$$

then

$$\frac{\mathrm{d}W^{i+1}}{\mathrm{d}t} = \mathrm{f}(W^{i}, A^{i}, E^{i}, n^{i}) + \frac{\partial f^{i}}{\partial W^{i}}(W^{i+1}-W^{i}) + \frac{\partial f^{i}}{\partial A^{i}}(A^{i+1}-A^{i}) + \frac{\partial f^{i}}{\partial E^{i}}(E^{i+1}-E^{i}) + \frac{\partial f^{i}}{\partial n^{i}}(n^{i+1}-n^{i}) + \text{ignored higher-order terms} \tag{10}$$

where the i superscripts indicate the particular iteration.

In expanded form, Eqn. (10) becomes

$$\frac{\mathrm{d}W^{i+1}}{\mathrm{d}t} = -\Big[A^{i}\,e^{-E^{i}/RT}\,(W^{i})^{n^{i}} + n^{i}A^{i}\,e^{-E^{i}/RT}\,(W^{i})^{n^{i}-1}\,(W^{i+1}-W^{i}) + e^{-E^{i}/RT}\,(W^{i})^{n^{i}}\,(A^{i+1}-A^{i}) - \frac{A^{i}}{RT}\,e^{-E^{i}/RT}\,(W^{i})^{n^{i}}\,(E^{i+1}-E^{i}) + A^{i}\,e^{-E^{i}/RT}\ln W^{i}\,(W^{i})^{n^{i}}\,(n^{i+1}-n^{i})\Big] \tag{11}$$

$$\frac{dA^{i+1}}{dt} = 0 \tag{12}$$

$$\frac{dE^{i+1}}{dt} = 0 \tag{13}$$

$$\frac{dn^{i+1}}{dt} = 0 \tag{14}$$

The iterative procedure is initiated by assuming values of A^0, E^0, and n^0 and solving Eqn. (4), by the Runge–Kutta numerical procedure, for $W^0(t)$. Setting $i = 0$, the linear differential Eqns. (11)–(14) are solved for $W^1(t)$, A^1, E^1, and n^1 by the procedure of forming a particular and homogeneous solution.

The solution of Eqn. (11) can now be represented in the form

$$W^{i+1}(t) = p^{i+1}(t) + \alpha_1^{i+1}\, h_1^{i+1}(t) + \alpha_2^{i+1}\, h_2^{i+1}(t) + \alpha_3^{i+1}\, h_3^{i+1}(t) \tag{15}$$

where α_1^{i+1} are constants to be determined. Thus,

$$\frac{dp^{i+1}}{dt} = -\Bigg[A^i\, e^{-E^i/RT}\, n^i\, (W^i)^{n^i-1}\, (p^{i+1} - W^i) + (W^i)^{n^i} A^i\, e^{-E^i/RT}\left(-\frac{1}{RT}\right)(-E^i) + A^i\, e^{-E^i/RT}\, (W^i)^{n^i} \ln(W^i)(-n^i)\Bigg] \tag{16}$$

and $p^{i+1}(0) = W(0)$, also

$$\frac{dh_1^{i+1}}{dt} = -\Bigg[A^i\, e^{-E^i/RT}\, n^i\, (W^i)^{n^i-1}\, (h_1^{i+1}) + (W^i)^{n^i}\, e^{-E^i/RT}\, (A^{i+1}) + (W^i)^{n^i} A^i\, e^{-E^i/RT}\left(-\frac{1}{RT}\right)(E^{i+1}) + A^i\, e^{-E^i/RT}\, (W^i)^{n^i} \ln(W^i)(n^{i+1})\Bigg] \tag{17}$$

The following convenient values of initial conditions are chosen: $h_1^{i+1}(0) = 0$; $A^{i+1}(0) = 1$; $E^{i+1}(0) = 0$; and $n^{i+1}(0) = 0$.
Similarly,

$$\frac{dh_2^{i+1}}{dt} = -\Bigg[A^i\, e^{-E^i/RT}\, n^i\, (W^i)^{n^i-1}\, (h_2^{i+1}) + (W^i)^{n^i}\, e^{-E^i/RT}\, (A^{i+1}) + (W^i)^{n^i} A^i\, e^{-E^i/RT}\left(-\frac{1}{RT}\right)(E^{i+1}) + A^i\, e^{-E^i/RT}\, (W^i)^{n^i} \ln(W^i)(n^{i+1})\Bigg] \tag{18}$$

with $h_2^{i+1}(0) = 0$; $A^{i+1}(0) = 0$; $E^{i+1}(0) = 1$; and $n^{i+1}(0) = 0$.

Also

$$\frac{\mathrm{d}h_3^{i+1}}{\mathrm{d}t} = -\left[A^i \mathrm{e}^{-E^i/RT}\, n^i (W^i)^{n^i-1} (h_3^{i+1}) + (W^i)^{n^i} \mathrm{e}^{-E^i/RT} (A^{i+1}) + \right.$$

$$\left.(W^i)^{n^i} A^i \mathrm{e}^{-E^i/RT}\left(-\frac{1}{RT}\right)(E^{i+1}) + A^i \mathrm{e}^{-E^i/RT} (W^i)^{n^i} \ln (W^i)(n^{i+1})\right] \qquad (19)$$

with $h_3^{i+1}(0) = 0$; $A^{i+1}(0) = 0$; $E^{i+1}(0) = 0$; $n^{i+1}(0) = 1$.

With $i = 0$, Eqns. (16), (17), (18), and (19) may be solved by the Runge–Kutta 4th-order method for $p^1(t)$, $h_1^1(t)$, $h_2^1(t)$, and $h_3^1(t)$. The constants α_j^{i+1} are determined for each iteration such that the objective function, Q, is minimized.

$$Q = \sum_{j=1}^{k} \left[W^{i+1}(t_j) - W_{j,\mathrm{DATA}}\right]^2 \qquad (20)$$

where $W^{i+1}(t_j)$ are the computed points and $W_{j,\mathrm{DATA}}$ are the corresponding data points for the particular times.

For $i = 0$, the objective function becomes,

$$Q_1 = \sum_{j=1}^{k} \left[p^1(t_j) + \alpha_1^1 h_1^1(t_j) + \alpha_2^1 h_2^1(t_j) + \alpha_3^1 h_3^1(t_j) - W_{j,\mathrm{DATA}}\right]^2 \qquad (21)$$

For a minimum Q_1

$$\frac{\partial Q_1}{\partial \alpha_1^1} = 0; \frac{\partial Q_1}{\partial \alpha_2^1} = 0; \text{ and } \frac{\partial Q_1}{\partial \alpha_3^1} = 0, \qquad (22)$$

or

$$\sum_{j=1}^{k} \left[[p^1(t_j) + \alpha_1^1 h_1^1(t_j) + \alpha_2^1 h_2^1(t_j) + \alpha_3^1 h_3^1(t_j) - W_{j,\mathrm{DATA}}]\, h_1^1(t_j)\right] = 0 \quad (23)$$

$$\sum_{j=1}^{k} \left[[p^1(t_j) + \alpha_1^1 h_1^1(t_j) + \alpha_2^1 h_2^1(t_j) + \alpha_3^1 h_3^1(t_j) - W_{j,\mathrm{DATA}}]\, h_2^1(t_j)\right] = 0 \quad (24)$$

$$\sum_{j=1}^{k} \left[[p^1(t_j) + \alpha_1^1 h_1^1(t_j) + \alpha_2^1 h_2^1(t_j) + \alpha_3^1 h_3^1(t_j) - W_{j,\mathrm{DATA}}]\, h_3^1(t_j)\right] = 0 \quad (25)$$

Eqns. (23), (24), and (25) are solved simultaneously for α_1^1, α_2^1, and α_3^1 using experimental values of $W_{j,\mathrm{DATA}}$ at t_j, and the computed p^1, h_1^1, h_2^1, h_3^1 at the $(k)t_j$ values. The resulting α values are related to the next set of kinetic parameters as follows: $\alpha_1^1 = A^1$, $\alpha_2^1 = E^1$, and $\alpha_3^1 = n^1$.

The iterations are continued until the parameters A, E, and n converge to within reasonable tolerances. When programmed for a digital computer, *e.g.*, the Univac 1108, the computations are extremely rapid. Data from more than one thermogram may be utilized. In this case a set of equations, one for each thermogram, of the form of Eqn. (11) are solved, and the objective function in Eqn. (20) is expanded to include all data sets.

Convergence of the quasilinearization technique given above is the major difficulty in its application. Realizing that a good initial guess of the values of the constants is necessary for convergence, we have used crude graphical methods to yield preliminary values. Probability of convergence is also enhanced if one of the parameters is constrained until the others have reached an optimized value. The concept of constrained parameters permits a variety of calculation strategies, each of which should converge to the same result. Of course, the required computer time can vary significantly, depending upon the strategy chosen.

Many of the problems associated with convergence in non-linear curve fitting can be reduced through reparameterization. Several different techniques of reparameterization have been published[6,7], and Kittrell[8] has discussed their application to kinetic analysis. Specifically in the case of a simple Arrhenius model

$$k = A\,\mathrm{e}^{-E/RT} \tag{26}$$

estimation of the two parameters from experimental data may yield a contour of convergence on a sum-of-squares surface which is very restricted. Convergence of an iterative routine for such a system may be slow or nonexistent. Experience seems to indicate that kinetic models should be reparameterized by a redefinition of the independent variables. Specifically, Kittrell recommends that the exponential parameter $k = A\,\mathrm{e}^{-E/RT}$ be redefined as

$$k = \bar{A}\,\mathrm{e}^{+[E/R(1/T-1/\bar{T})]} \tag{27}$$

where

$$\bar{A} = A\,\mathrm{e}^{-E/R\bar{T}} \tag{28}$$

We have taken the value of $\bar{T}$ as the temperature at the point of maximum rate of weight loss.

These modifications, which are mathematically equivalent to the original expression, transform the contour of convergence. Parameters $\bar{A}$ and E are obtained more readily, initial estimates are less critical, and convergence is more rapid. The application of this form of reparameterization to the quasilinearization equations is straightforward.

It is occasionally obvious from inspection of a thermogram that more than a single weight-loss mechanism is occurring. The extension of the quasilinearization technique to a two-mode model illustrates in general the procedure for handling multiple modes.

It has been assumed frequently that the total weight loss of a sample is the sum of two independent parallel reaction mechanisms, each associated with a fraction of the original sample weight[9]. Thus,

$$-\frac{\mathrm{d}W^{i+1}}{\mathrm{d}t} = \frac{-\mathrm{d}W_1^{i+1}}{\mathrm{d}t} + \frac{-\mathrm{d}W_2^{i+1}}{\mathrm{d}t} = (W_1^i)^{n_1^i}\,A_1^i\,\mathrm{e}^{-E_1^i/RT} + (W_2^i)^{n_2^i}\,A_2^i\,\mathrm{e}^{-E_2^i/RT} \tag{29}$$

where $W = \frac{w - w_r}{w_0}$, $W_1 = \frac{w_1 - w_{r,1}}{w_{0,1}}$, $W_2 = \frac{w_2 - w_{r,2}}{w_{0,2}}$,

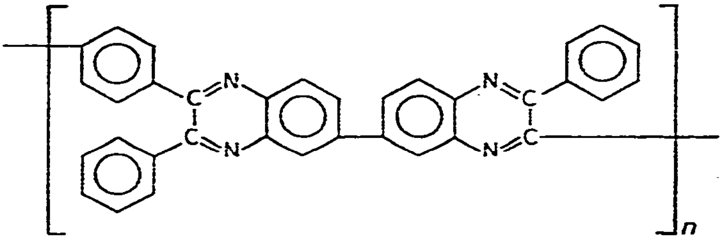
and $w_1 + w_2 = w$, $w_{0,1} + w_{0,2} = w_0$.

In this case the approach is to determine independently the particular and homogeneous solutions of each mode and consequently $W_1(t)$ and $W_2(t)$. Using the defining equations, w_1 and w_2 are calculated.

Graphical integration of a reaction peak on a plot of rate-of-weight-loss *vs.* temperature yields values of $w_i - w_{r,i}$. In order to obtain values of w_i, an assumption is usually made as to the value of $w_{r,i}$. Generally it is assumed that one reaction produces only gaseous products and the other, therefore, yields all the char residue. Using this assumption, or any other justified by experimental evidences, values of w_i are calculated. The combination of w_1 and w_2 yields $w^{i+1}(t)$, which is used in the calculation of the objective function Q. With these modifications the solution proceeds as outlined for a single mode.

APPLICATION OF THE QUASILINEARIZATION METHOD

Experimental TG data were obtained for a phenyl-substituted poly-quinoxaline polymer using a Cahn RG Electrobalance. The polymer was prepared by Wrasidlo and Augl of the U.S. Naval Ordnance Laboratory by one-step solution condensation of 3,3'-diaminobenzidine with 1,5-bis(phenylglyoxaloyl)benzene at room temperature. An infrared spectra of the polymer showed no carbonyl band and no residual NH band, thus indicating complete cyclization to give:



The resin sample as received was a light yellow flocculant powder. TG data were obtained on the polymer as received with no prior resin advancement.

A dynamic thermogram obtained with a non-flow helium atmosphere is shown in Fig. 1. The temperature-rise-rate employed in this test was 10°C/min. Numerical differentiation of discretized data produced the rate-of-weight-loss curve shown in Fig. 2. The appearance of two reaction peaks, which are reasonably separated, presented a good opportunity to test the application of the quasilinearization method to a two-mode model as described by Eqn. (29).

Several computational strategies using the quasilinearization method were tried before convergence was obtained in the iterative calculations, leading to optimal

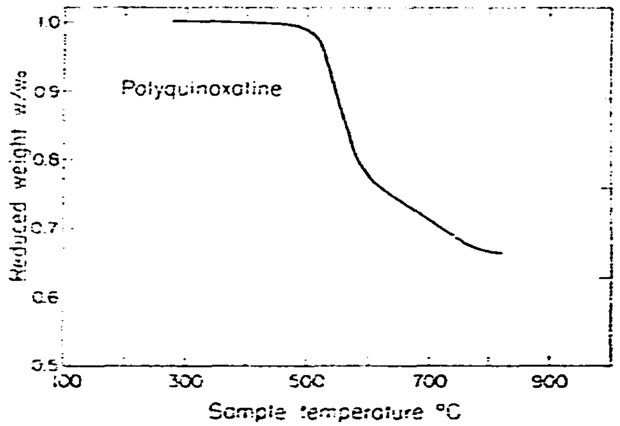


Fig. 1. Dynamic thermogram for polyquinoxaline at 10°C/min in non-flowing helium.

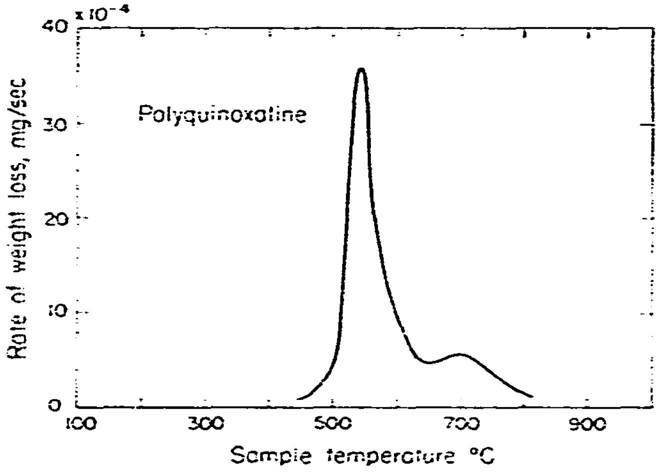


Fig. 2. Rate of weight loss for polyquinoxaline in non-flowing helium.

values of the kinetic parameters. As a first attempt, graphically obtained values of kinetic parameters were used as the initial approximations in an unrestrained calculation. This calculation failed to be sufficiently stable to permit convergence, apparently because of the very sensitive interaction between the two reaction modes.

As a second trial, it was attempted to optimize the parameters of the second peak with those of the first peak, with the order of reaction of the second, n_2, held constant at an assumed constrained value. The reverse calculation was also tried holding n_1 constant. While these approaches did lead to some convergent values the sensitivity of interaction between the parameters made optimization of the combined modes very laborious.

The third and best approach tried was to optimize first the kinetic parameters of the first reaction peak using only data taken before the second reaction peak became activated. However, it was necessary to constrain n_1 during these calculations. Graphical values of n_1 had been obtained which varied from 1.6 to 2.0. Computer calculations using the quasilinearization method were carried out for various constrained values of n_1. The resulting optimal values of A_1 and E_1 are shown in Table I.

TABLE I

CONVERGENT KINETIC PARAMETERS FOR THE FIRST REACTION PEAK OF POLYQUINOXALINE

Constrained n_1	A_1 *(sec^{-1})*	E_1 *(cal)*	*Sum of least squares*
1.0	7.050×10^{9}	46,627	0.1328×10^{-1}
1.6	2.680×10^{13}	58,369	0.6686×10^{-2}
1.7	1.102×10^{14}	60,394	0.5973×10^{-2}
1.9	1.929×10^{15}	64,502	0.4787×10^{-2}
2.0	8.212×10^{15}	66,585	0.4299×10^{-2}
3.0	2.980×10^{22}	88,445	0.1956×10^{-2}

The least squares fit of the data shown in Table I seem to justify use of an n even larger than 3.0. However, the convergent parameters for an n of 3.0 seemed to predict a greater weight loss near the end of the first reaction than that actually observed.

Having now an indication of the magnitude of the parameters for the first peak, values of n_2, A_2 and E_2 for the second peak were sought while the parameters for the first were held constant. Combinations of n_1 and n_2 were tried with the result that n_2 was found to be near 2.0. Values of n_2 either greater or less than 2.0 seemed to lead to poor agreement with the data.

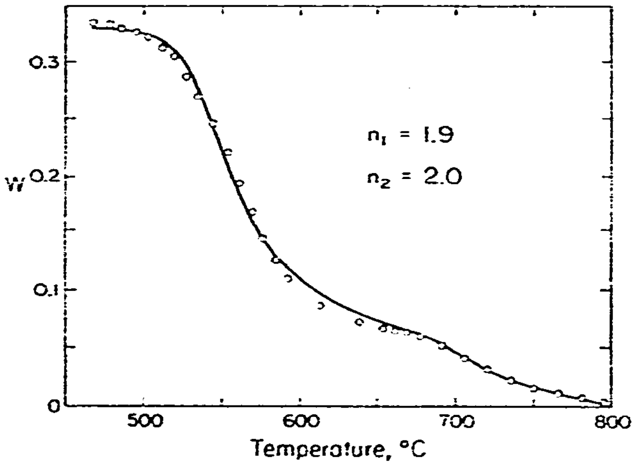


Fig. 3. A comparison of data and numerically optimized results for polyquinoxaline.

As a final step in applying the two-mode model, both reaction peaks were optimized simultaneously. In this case it was still necessary to constrain the values of n_1 and n_2. The results of several combinations are presented in Table II to illustrate the trends. Values of 3.1 for n_1 and 2.0 for n_2 appeared to give the best fit of the data.

Fig. 3 illustrates a comparison of data and computed points from optimized kinetic parameters for $n_1 = 1.9$ and $n_2 = 2.0$. Fig. 4 shows a similar plot for $n_1 = 3.0$ and $n_2 = 2.0$. As can be seen in Fig. 4, the parameters determined by quasilinearization describe the complex dynamic reaction curve very well. The fit of the parameters shown in Fig. 3 is obviously inferior to that shown in Fig. 4 and yet the over-all conformity is reasonably good. Such an observation emphasizes the need for accurate data for use in determining kinetic parameters, since inconsistencies or scatter would seriously affect the final results.

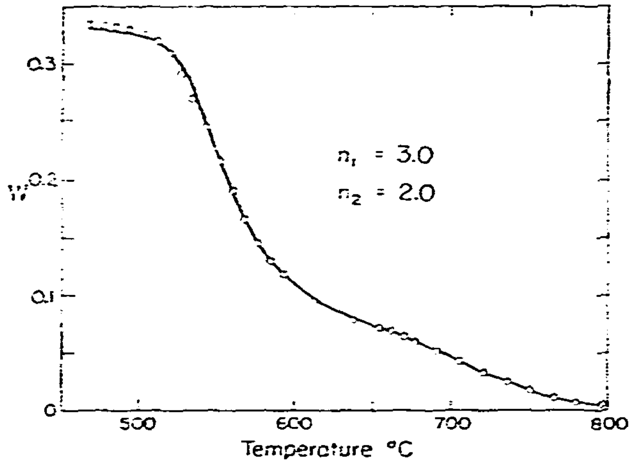


Fig. 4. A comparison of data and numerically optimized results for polyquinoxaline.

TABLE II

CONVERGENT KINETIC PARAMETERS FOR POLYQUINOXALINE PYROLYSIS

n_1	A_1 (sec^{-1})	E_1 (cal)	n_2	A_2 (sec^{-1})	E_2 (cal)	Sum of least squares
2.0	1.242×10^{22}	84,049	1.9	7.195×10^{11}	62,109	0.1432×10^{-2}
3.0	1.394×10^{22}	87,232	2.1	1.161×10^{13}	66,814	0.1425×10^{-2}
2.9	2.574×10^{21}	84,758	2.0	3.836×10^{12}	65,028	0.1523×10^{-2}
3.0	1.474×10^{21}	87,104	2.0	1.020×10^{13}	64,445	0.1426×10^{-2}
3.1	6.818×10^{22}	89,545	2.0	2.171×10^{12}	63,889	0.1353×10^{-2}

In all of the quasilinearization calculations discussed above for polyquinoxaline it was assumed that the material was composed of two parts which reacted independently to form both gas and char. It was further assumed that the starting material in both reactions produced the same fractional char yield as was determined for the combined reaction from the dynamic thermogram. Other assumed mechanisms have been evaluated by Burningham[10] using quasilinearization.

CONCLUSION

Mathematical analysis of thermogravimetric data by the technique of quasilinearization offers several significant advantages over many commonly employed methods. Quasilinearization, as developed in this paper, has been successfully applied to the kinetic analysis of para-polyphenylene, polyquinoxaline and polyimide polymers. Only the polyquinoxaline example is included here. Only a few of the many possible applications of this powerful technique to the kinetics of polymer decomposition have been explored.

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