Thermochimica Acta, 95 (1985) 41–58
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A COMPUTER PROGRAM SYSTEM FOR KINETIC ANALYSIS OF NON-ISOTHERMAL THERMOGRAVIMETRIC DATA.
II. GENERALIZED KINETIC ANALYSIS AND APPLICATION TO COAL PYROLYSIS *

JOHN P. ELDER **

Institute for Mining and Minerals Research, Kentucky Center for Energy Research Laboratory, P.O. Box 13015, Lexington, KY 40512 (U.S.A.)

(Received 25 April 1985)

ABSTRACT

A FORTRAN program is presented which enables the kinetic analysis of extent and rate of reaction data resulting from transposed experimental TG/DTG data obtained under non-isothermal conditions. This software allows one to perform Arrhenius, Friedman and Kissinger analyses for up to nine different solid-state rate-controlling reactions, including *n*th order, Avrami–Erofeev, phase boundary movement and diffusional models. Data from an investigation of the pyrolysis of a bituminous coal serve as an example of the application of the program.

INTRODUCTION

In 1980, Zsako and Zsako [1] described a FORTRAN program system for the determination of kinetic parameters from non-isothermal thermogravimetric (NITG) data descriptive of solid-state degradative reactions. Their methods were based upon using the integral form of the basic rate equation. However, the procedure was limited to *n*th order reactions. Recently, Reich and Stivala [2] presented a program, written in BASIC, for such analyses. They, too, utilized the integral approach, but have extended it to cover up to ten different kinetic models of the type discussed by Brown et al. [3].

Recently, the author has presented a computerized approach to the simulation of multiple reaction scheme models involving either mutually independent or parallel competitive first-order single reactions [4]. This software has since been extended to cover other solid-state kinetic models [5]. The modified Kissinger equation [6] has been shown to be generally

---

* To be presented at the 14th North American Thermal Analysis Society Conference, San Francisco, CA, 15–18 September 1985.

** Present address: Merck and Co. Inc., P.O. Box 2000, R50D-101, Rahway, NJ 07065, U.S.A.

0040-6031/85/$03.30

applicable for the analysis of thermally induced extent and rate of reaction data, irrespective of the kinetic model employed [7]. Furthermore, the resulting kinetic parameters are in full agreement with those obtained by using the Friedman procedure, namely Arrhenius analysis at constant extent of reaction. It has also been pointed out [7] that one is advised to proceed with caution in assessing the results of Arrhenius analyses of NITG data.

A natural extension of this work is to utilize the developed algorithms and mathematical routines to construct a software system capable of performing kinetic analyses of extent and rate of reaction values, obtained from experimental NITG data, transposed by program TGDATCON, as described in part I. As has recently been pointed out [8], in studying the pyrolysis of bituminous coals by NITG, experimental measurements should be made at heating rates greater than 5°C min^{-1}. In order to accomplish this, and obtain meaningful data over as wide a heating rate range as possible, it is imperative that a sample temperature control of ± 2°C be maintained over the entire working temperature range of the degradative process. Such a method has been developed for the Perkin-Elmer TGS-2/System 4 thermogravimetric analyzer [9].

This paper describes a general FORTRAN computer program for the kinetic analysis of transposed NITG data, obtained over a wide range of heating rates, using the Arrhenius, Friedman and Kissinger procedures.

SUMMARY OF KINETIC EQUATIONS

The rate of a thermally induced reaction is assumed to follow the general relationship

$$\mathrm{d}\alpha/\mathrm{d}t = AT^m\,\mathrm{e}^{-E/RT}\mathrm{f}(\alpha) \tag{1}$$

The integral form is given by eqn. (2) with the exponential integral p-function given by eqn. (3) [6].

$$\mathrm{F}(\alpha) = A/[\beta(m+1)](E/R)^{m+1}\mathrm{p}_m(E/RT) \tag{2}$$

$$\mathrm{p}_m(E/RT) = \exp(-E/RT)(RT/E)^{m+2}\gamma_m(E/RT) \tag{3}$$

α is the dimensionless extent of reaction, $\mathrm{f}(\alpha)$ is the kinetic model α dependency with T, R, A and E having their usual significance (see list of symbols). The Arrhenius equation is then given by

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/T^m\mathrm{f}(\alpha)] = \ln A - E/RT \tag{4}$$

The simple and corrected form of the Friedman equations are given by eqns. (5a) and (5b), respectively.

$$\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha = \ln[AT^m\mathrm{f}(\alpha)] - E/RT \tag{5a}$$

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)_\alpha/T^m\mathrm{f}(\alpha)] = \ln A - E/RT \tag{5b}$$

TABLE 1

Kinetic model parameters

Model [3]	Mode	f(α)	F(α)	$-$f′(α_{max})	α_{max}
F, 1	1	$1-\alpha$	$-\ln(1-\alpha)$	1	$1-e^{-\eta}$
F, n	2	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$	$\eta+n(1-\eta)$	$1-\{1-[(n-1)/n]\eta\}^{1/(n-1)}$
A2, A3 [a]	3, 4	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	$[-\ln(1-\alpha)]^{1/n}$	$[n\eta^n(n+\eta-1)^{1/n}$	$1-e^{(1-n-\eta)/n}$
R2, R3 [a]	5, 6	$n(1-\alpha)^{(n-1)/n}$	$1-(1-\alpha)^{1/n}$	$n+\eta-1$	$1-[(n-1)/(n+\eta-1)]^n$
D2	7	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	$1/(1-\alpha_{max})[-\ln(1-\alpha_{max})]^2$	See Elder [6]
D3	8	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$	$\eta[(\eta+1/2)/(\eta-1/2)]^2$	$1-(\eta+1/2)^{-3}$
D4	9	$3/2[(1-\alpha)^{-1/3}-1]$	$1-2\alpha/3-(1-\alpha)^{2/3}$	$1/2(1-\alpha_{max})^{2/3}[(1-\alpha_{max})^{1/3}-1]^2$	$1-[1/6\eta+(1/36\eta^2+1/6\eta)^{1/2}]^3$

[a] $n = 2$ and 3, respectively.

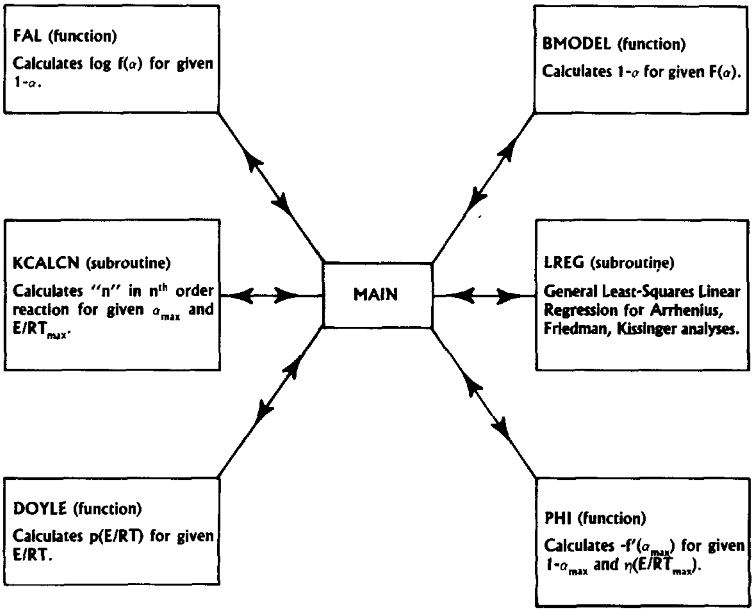

Fig. 1. Schematic of program TGKIN.

The generalized Kissinger equation is given [6,7] by eqn. (6) with the correction term given by eqn. (7)

$$\ln(\beta/T_{\max}^{m+2}) = \ln(AR/E) + \ln \phi_m(\alpha_{\max}) - E/RT_{\max} \qquad (6)$$

$$\phi_m(\alpha_{\max}) = -\mathrm{f}'(\alpha_{\max})/(1 + mRT_{\max}/E) \qquad (7)$$

The relevant variables $\mathrm{f}(\alpha)$, $\mathrm{F}(\alpha)$, $-\mathrm{f}'(\alpha_{\max})$ and $\alpha_{\max}$ are listed in Table 1 for nine kinetic models. The η-function appearing in this table is given by eqn. (8) where $x = E/RT_{\max}$

$$\eta_m(E/RT_{\max}) = (1 + m/x)\mathrm{p}_m(x)x^{m+2}\,\mathrm{e}^{x} \qquad (8)$$

The cubic approximation used for the p- and γ-functions in eqn. (3) has been discussed previously [6].

PROGRAM TGKIN

Figure 1 shows a schematic of the general kinetic analysis FORTRAN program, TGKIN. (See part I for details of the computer system used.) The FAL sub-function is used to generate $\mathrm{f}(\alpha)$, according to Table 1, to be used in its logarithmic form in the Arrhenius and Friedman analyses. BMODEL essentially performs the inverse function, calculating $1-\alpha$ values for any given $F(\alpha)$. The DOYLE sub-function allows the determination of the exponential integral for a given E/RT value using the cubic approximation [6]. Sub-function PHI is used to calculate $-f'(\alpha_{\max})$ as shown in Table 1 and, hence, the ϕ-function from eqn. (7) for use in the generalized Kissinger analysis. For *n*th order reactions, sub-routine KCALCN is an iterative procedure for determining n knowing $E/RT_{\max}$ and $\alpha_{\max}$ according to the $\alpha_{\max}-n$ relationship given in Table 1, with the η-function given by eqn. (8). Finally, LREG is a least-squares linear regression routine used in all analyses.

Figure 2 shows the flow chart of the main program, and for the most part is self-explanatory. For all models, with the exception of *n*th order, namely mode 2 (see Table 1), only one Arrhenius analysis is performed. For *n*th order model calculations, one initially performs a Kissinger analysis without the correction term, using the Kissin input file (output file from program TGDATCON, see part I). As has been shown [7], the inclusion of the correction term has only a minor effect on the value of E for *n*th order reactions, and therefore the value of n may be calculated accurately using the Kissinger E value. An Arrhenius analysis is first performed assuming a first-order model. Using the resulting E value, $E/RT_{\max}$ is set and an n-value calculated for use in a second Arrhenius analysis. Then, if desired, a third analysis is performed using the Kissinger-derived n-value. These analyses employ data stored in the Alpha file, the program TGDATCON output file. A certain latitude is built into the program, allowing one to control the accuracy of the regression, and to define the region of the input data to be used. The integral value of the percentage allowable deviation from linearity in a continuing regression following the initial regression over defined data limits is set. The most effective way of defining these limits is by setting the reaction-rate values at which the analysis is to be initiated and concluded. The start/end $d\alpha/dt$ values are defined as percentages of $(d\alpha/dt)_{\max}$. In order to be able to differentiate between start/end values prior to or following the maximum rate of reaction, a special code is used. For values subsequent to the peak, the code 200 minus the desired value is used. For example, if it is desired to allow a 10% deviation from linearity in a continuing regression following the initial regression for $d\alpha/dt$ from 5% of the maximum rate prior to the peak to 30% of the maximum rate following the peak, the code numbers 10, 5 and 170 are entered upon request from the program. Program feedback allows the operator to repeat the Arrhenius analyses ad infinitum, selectively varying the start/end limits as required for an optimal output, usually indicated by the regression correlation coefficient close to unity. Details of the analyses, including the table of input parameters for eqn. (4), and a table of actual and calculated $1-\alpha$ values and their relative difference may be printed out at set temperature intervals, if desired.

In order to perform Friedman analyses, namely, Arrhenius analyses at constant α, since there is no certainty that input data has been obtained at precisely defined extents of reaction, this data must be calculated. The rates and temperatures of reaction are computed by a linear interpolation between values corresponding to the two closest α values prior and subsequent to the required extent of reaction. The reaction rate is assumed to be a linear function of temperature over the small interval encompassing the required

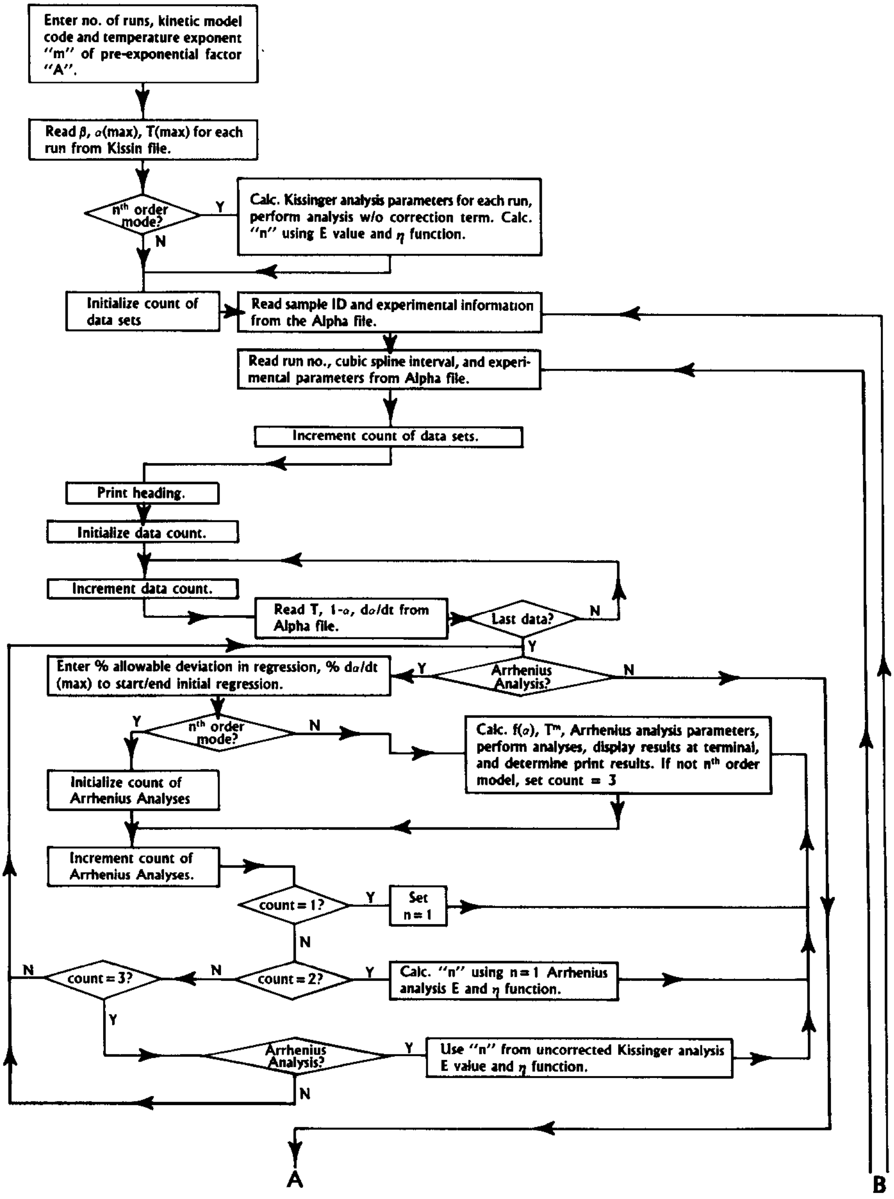

Fig. 2. Detailed flow chart of program TGKIN.

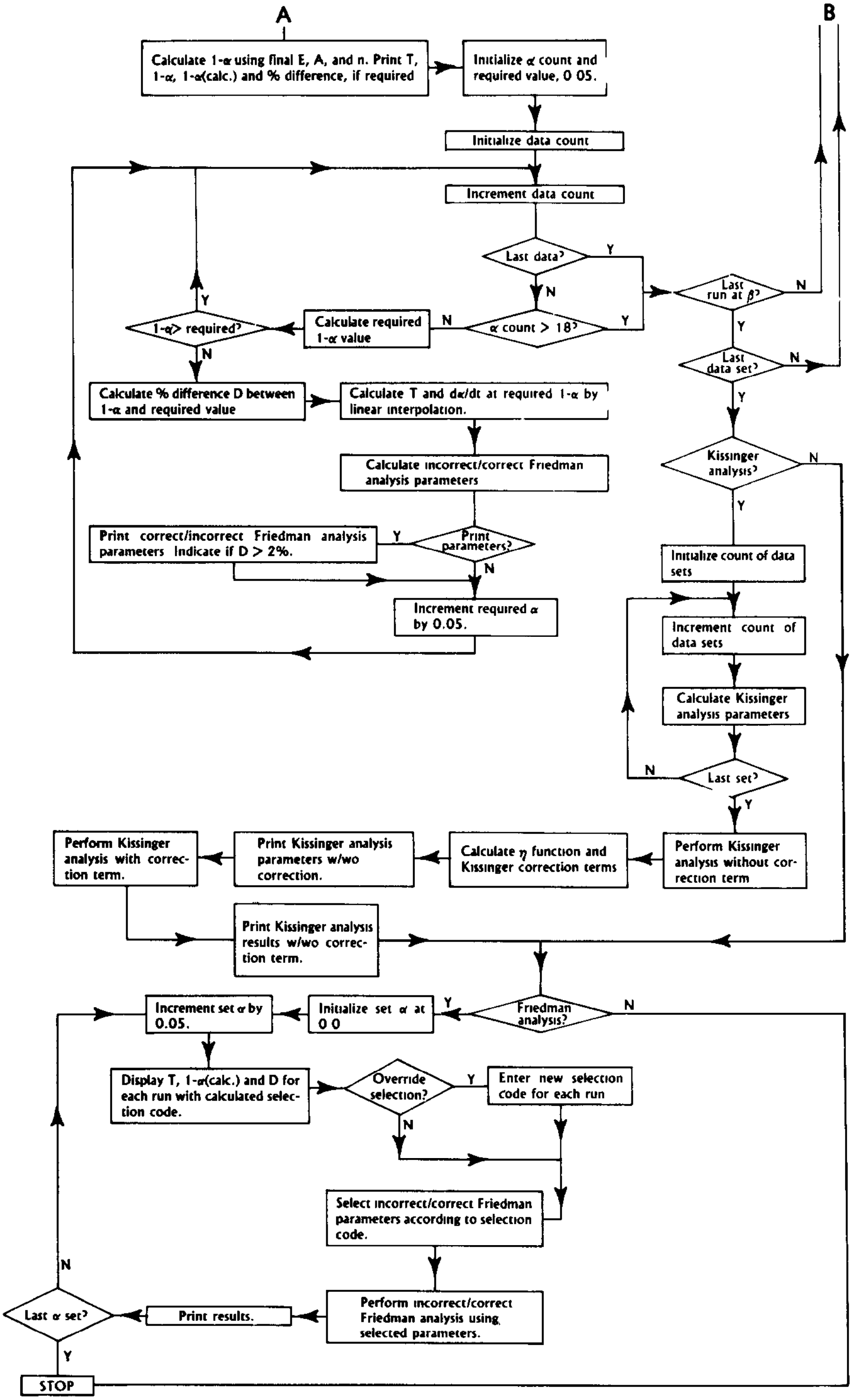

Fig. 2 (continued).

extent of reaction. The success of the interpolation is therefore dependent upon the proximity of the two actual α values to the required value. This is to a large degree dependent upon the nature of the material under investigation and the TG signal noise. The calculated $d\alpha/dt$ and T values are stored for later use and also employed to generate the input parameters for the Friedman equations (5a, 5b). If desired, these parameters may be printed out and if the relative difference, D, between either the two closest actual and the required α values is $\geqslant 2\%$, this is so noted in the printout. These interpolations are carried out for fixed extents of reaction ranging from 5 to 95% inclusive, at 5% intervals. When all transposed experimental data at the several heating rates have been considered, and the Kissinger analyses performed, the Friedman analyses are carried out. At each of the fixed extents of reaction, the two α values closest to the set value and the calculated reaction temperature for each run at each heating rate are displayed at the video terminal. The operator can now select which are to be used in the subsequent regressions, according to eqns. (5a) and (5b).

KINETIC ANALYSIS OF COAL PYROLYSIS DATA

$1-\alpha$ and $d\alpha/dt$ values for a Western Kentucky #9, −60 mesh high volatile (HV) B bituminous coal from 1 to 150°C min^{-1} are shown in Figs. 3 and 4, respectively. These values previously introduced [10] were transposed by program TGDATCON. The overall shape of these curves exhibits fea-

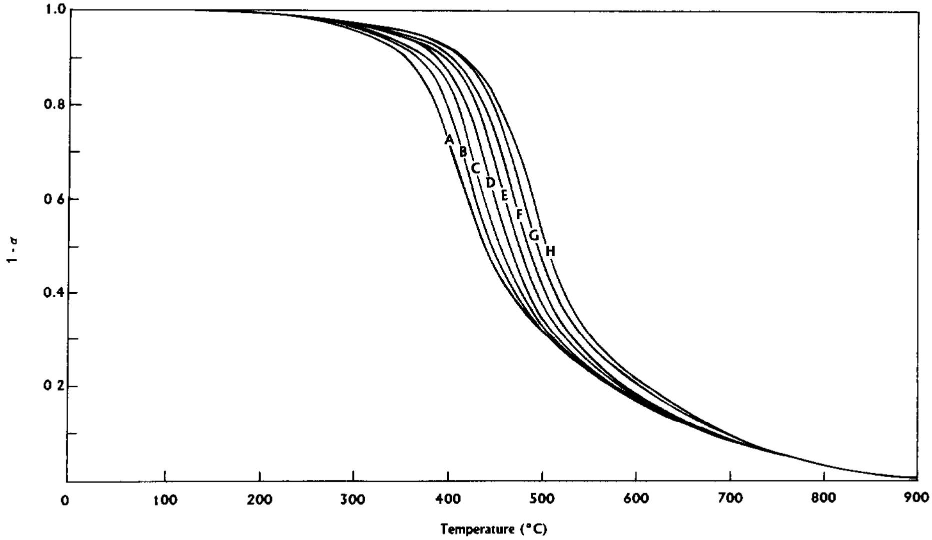

Fig. 3. Western Kentucky #9 high volatile B bituminous coal $1-\alpha$ curves at (A) 1; (B) 2.5; (C) 5; (D) 10; (E) 20; (F) 50; (G) 75; (H) 150°C min^{-1}.

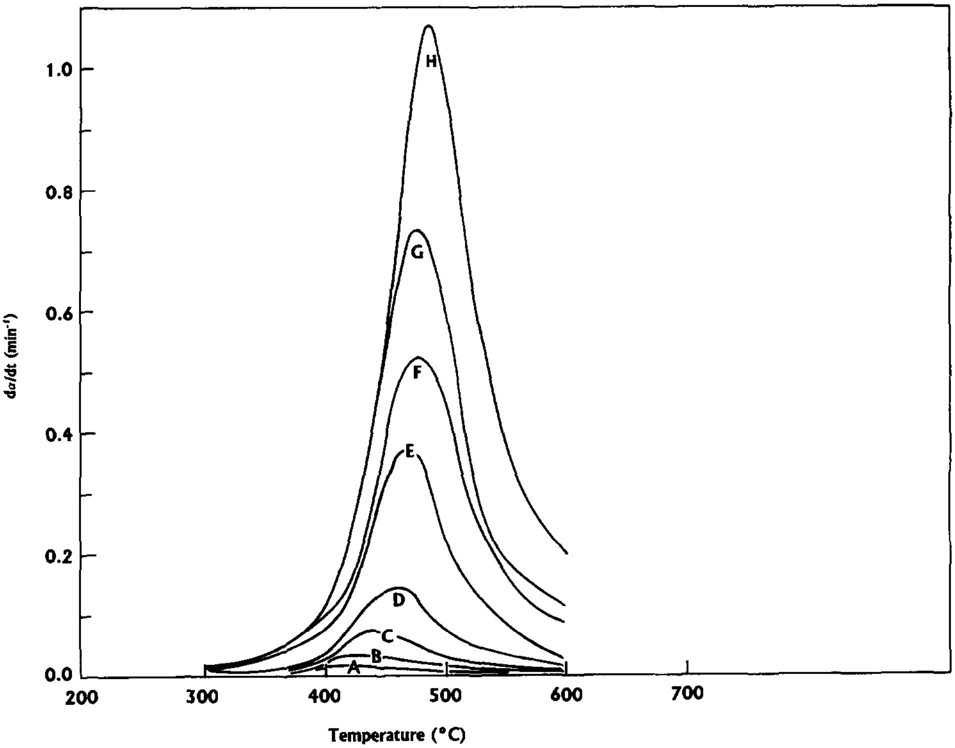

Fig. 4. Western Kentucky #9 high volatile B bituminous coal dα/dt curves at (A) 1; (B) 2.5; (C) 5; (D) 10; (E) 20; (F) 50; (G) 75; (H) 150°C min^{-1}.

tures indicative of different kinetic models [7]. The flat initial region, ca. 100–350°C, in Fig. 3 is typical of that predicted for a diffusion-controlled process, while the middle region, ca. 350–500°C, is typical of an nth order process. This, as has been pointed out [4], could be interpreted as characterizing the multiple effect of a number of mutually independent first-order reactions. This region, however, merges into a third region, ca. 500–600°C, which tails off in a manner characteristic also of an nth order reaction. Figure 5 shows for comparison the $1-\alpha$ curve at 5°C min^{-1} and that calculated (dashed line) from Arrhenius analysis kinetic parameters, which are summarized in Table 2. In all the calculations to be discussed, the pre-exponential factor temperature exponent, m, has been assumed to be zero. It should be noted that the data could equally well have been analyzed assuming m to be unity.

It is not possible to fit the region AB data to an nth order model. They are best analyzed in terms of either a surface (D2) or a bulk (D4) diffusion model, but it is not possible, in this particular instance, to differentiate between the two. This initial region, in which the rate only attains a value of 12% of maximum, covers the first 8% of the weight loss data. The regression is not perfect, as indicated by the correlation coefficient of 0.9698. However,

TABLE 2

Western Kentucky #9, −60 mesh HV B bituminous coal: Arrhenius analysis [a] kinetic parameters, $\beta = 5°\text{C min}^{-1}$, run #1

Region	$\frac{d\alpha/dt}{(d\alpha/dt)_{max}}$ (%)		Range				Model	n	E (kJ mol^{-1})	A (min^{-1})	CC [b]
			α		T (°C)						
	Start	End	Start	End	Start	End					
AB	0	12	0	0.08	100	353	D2		49.76	3.206	0.9698
							D4		49.85	0.731	0.9698
BC	12	159 [c]	0.08	0.66	353	496	F,n	1	69.83	4.777×10^3	0.8745
								4.26	169.65	6.537×10^{11}	0.9947
CD	159 [c]	185 [d]	0.66	0.85	496	607	F,n	4.26	106.09	1.897×10^7	0.9867

[a] 1% allowable deviation from linearity after initial regression.

[b] Correlation coefficient.

[c] 41% after peak attainment.

[d] 15% after peak attainment.

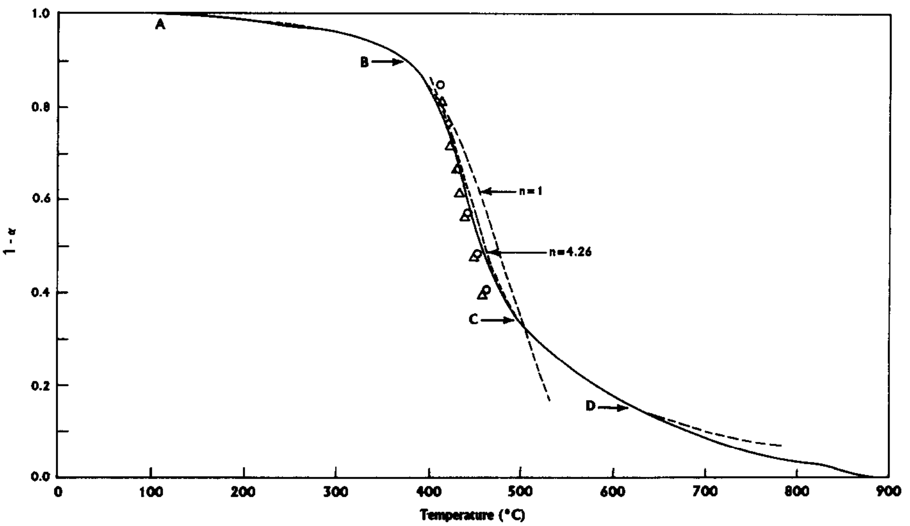

Fig. 5. Western Kentucky #9 high volatile B bituminous coal $1-\alpha$ data at 5° C min^{-1}. Calculated by Arrhenius analysis (------), by Kissinger analysis (○) and by Friedman analysis (△).

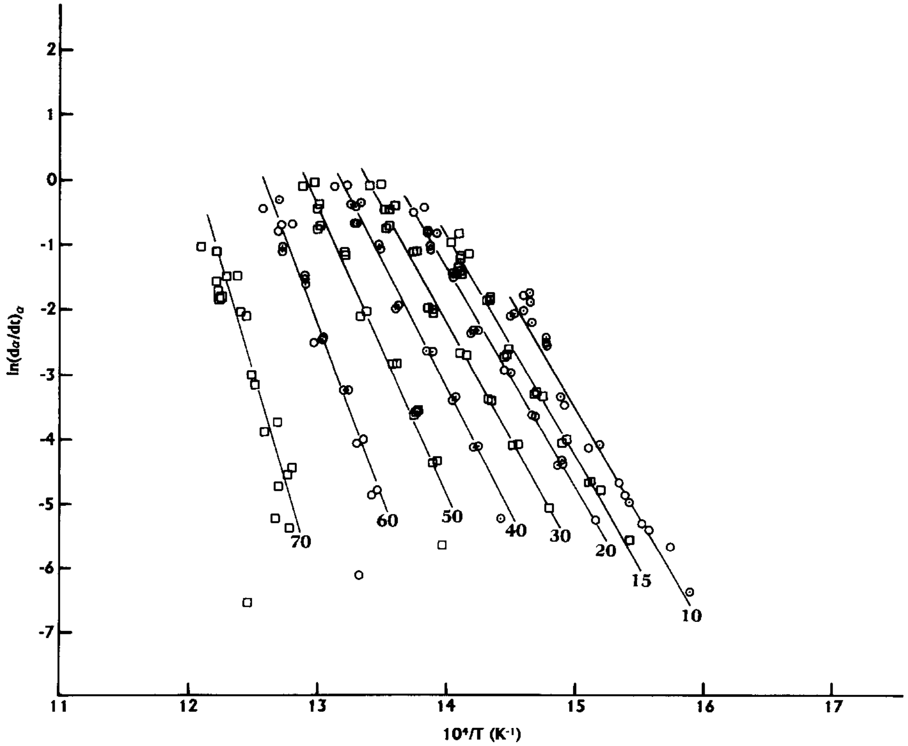

Fig. 6. Western Kentucky #9 high volatile B bituminous coal Friedman plots (eqn. 5a) at various percentage extents of reaction.

TABLE 3

Western Kentucky #9, −60 mesh HV B bituminous coal: comparison of actual and calculated extents of reaction, region AB, model D4

T (°C)	$1-\alpha$ (actual)	$1-\alpha$ (calc.)	% Change
110	0.9995	0.9980	0.15
120	0.9984	0.9972	0.12
130	0.9972	0.9966	0.06
170	0.9930	0.9930	0
180	0.9916	0.9917	−0.01
190	0.9896	0.9902	−0.06
220	0.9831	0.9845	−0.14
230	0.9805	0.9822	−0.17
240	0.9770	0.9796	−0.27
280	0.9694	0.9667	0.28
290	0.9672	0.9627	0.47
300	0.9635	0.9584	0.53
310	0.9581	0.9538	0.45
320	0.9515	0.9488	0.29
340	0.9369	0.9377	−0.09
350	0.9391	0.9317	−0.28

using the kinetic parameters for the D4 model, the calculated $1-\alpha$ values listed in Table 3 were obtained. The agreement with the actual values is excellent, and only in the region 230–270°C can the two be differentiated.

The major weight loss of degradative products, saturated and unsaturated hydrocarbon gases and volatile oils, oxides of carbon and perhaps some hydrogen, occurs in the region BC, 8–66% of the total extent of reaction. The rate of reaction, initially 12% of the maximum, increases, attains the maximum value and then decreases to 41% of maximum. As is obvious from Fig. 5, the usual assumption [11] of a first-order model for this complex multiple process is incorrect. The E and A values are very low and the regression correlation coefficient of 0.8745 is poor. Much better agreement between calculated and actual $1-\alpha$ values is obtained by using the Kissinger analysis-derived n value of 4.26, with the indicated Arrhenius kinetic parameters, 169.65 kJ mol^{-1} and 6.537×10^{11} min^{-1}. The regression correlation coefficient, 0.9947, is excellent. Over the entire heating rate range, 1–150°C min^{-1}, consistent kinetic parameter values are obtained for this region, namely $\bar{E} = 169.47$ kJ mol^{-1} with $\sigma = 0.21$ kJ mol^{-1}. As the heating rate increases from 1 to 150°C min^{-1}, the pre-exponential factor, A, increases from 4×10^{11} to 2×10^{12} min^{-1}, while the order of reaction, n, decreases from 5 to 2.7. However, these orders of reaction were based upon a Kissinger analysis derived E value, and it is here that an inconsistency emerges.

The β, $T_{\max}$ and $\alpha_{\max}$ input parameters (Kissin file) for the Kissinger

TABLE 4

Western Kentucky #9, −60 mesh HV B bituminous coal: Kissinger analyses

β (°C min^{-1})	n	T_{max} (°C)	α_{max}	$\ln(\beta/T_{max}^2)$	$\ln \phi_0(\alpha_{max})$	Corrected $\ln(\beta/T_{max}^2)$	$1/T$ (K^{-1})
Digital data							
1.0	5.000	404.0	0.3056	−13.0358	0.15204	−13.1878	1.477*E*−03
2.5	4.190	421.0	0.3362	−12.1691	0.12647	−12.2956	1.441*E*−03
2.5	4.210	419.0	0.3356	−12.1633	0.12680	−12.2901	1.445*E*−03
2.5	3.820	422.0	0.3530	−12.1720	0.11276	−12.2847	1.439*E*−03
5.0	4.260	429.0	0.3328	−11.4989	0.13074	−11.6296	1.424*E*−03
5.0	3.830	431.0	0.3522	−11.5045	0.11481	−11.6194	1.420*E*−03
5.0	3.850	431.0	0.3513	−11.5045	0.11558	−11.6201	1.420*E*−03
10.0	3.470	445.0	0.3704	−10.8508	0.10321	−10.9540	1.392*E*−03
10.0	3.440	443.0	0.3721	−10.8452	0.10170	−10.9469	1.396*E*−03
20.0	3.150	459.0	0.3879	−10.1962	0.09243	−10.2887	1.366*E*−03
20.0	3.860	455.0	0.3499	−10.1853	0.12043	−10.3057	1.373*E*−03
20.0	3.120	459.0	0.3901	−10.1962	0.09120	−10.2874	1.366*E*−03
50.0	3.101	468.0	0.3905	−9.3044	0.09165	−9.3960	1.349*E*−03
50.0	3.610	463.0	0.3622	−9.2908	0.11181	−9.4027	1.358*E*−03
50.0	3.590	464.0	0.3632	−9.2936	0.11118	−9.4047	1.357*E*−03
75.0	3.081	479.0	0.3913	−8.9284	0.09229	−9.0207	1.330*E*−03
75.0	3.200	477.0	0.3845	−8.9231	0.09703	−9.0201	1.333*E*−03
75.0	2.831	481.0	0.4077	−8.9337	0.08187	−9.0156	1.326*E*−03
100.0	2.970	481.0	0.3987	−8.6460	0.08782	−8.7338	1.326*E*−03
100.0	3.480	475.0	0.3683	−8.6300	0.10842	−8.7385	1.337*E*−03
100.0	3.000	476.0	0.3969	−8.6327	0.08847	−8.7212	1.335*E*−03
150.0	3.070	487.0	0.3917	−8.2564	0.09286	−8.3493	1.316*E*−03
150.0	2.724	485.0	0.4151	−8.2511	0.07770	−8.3288	1.319*E*−03

uncorrected: $E = 252.95$ kJ mol^{-1}; $A = 1.796E+18$ min^{-1}; corr. coeff. = −0.9907
corrected: $E = 255.64$ kJ mol^{-1}; $A = 2.547E+18$ min^{-1}; corr. coeff. = −0.9914

analyses are listed in the top section of Table 4 together with the Kissinger parameters. For comparison, the analog data are also tabulated. At heating rates $\leqslant 20$°C min^{-1} the two sets of data are in good agreement. However, at the higher heating rates, there is an ever-increasing difference in T_{max} and, therefore, the α_{max} values. This has a significant effect on the calculated kinetic parameters, E and A, and on the predicted reaction orders, n. The circles in the BC region of Fig. 5 are the $1-\alpha$ values calculated using the Kissinger parameters from the corrected analysis of the digital data, namely, $E = 255.66$ kJ mol^{-1} and $A = 2.547 \times 10^{18}$ min^{-1} with $n = 4.26$ ($\beta = 5$°C min^{-1}, run #1). Over the major part of this region, the values are in very good agreement with the input data. The discrepancy between the Kissinger and Arrhenius parameters is a problem which can only be solved after considering the results of the Friedman analyses.

Table 5 shows an example of the Friedman parameters to be used in

TABLE 4 (continued)

β (°C min^{-1})	n	$T_{\max}$ (°C)	$\alpha_{\max}$	$\ln(\beta/T_{\max}^2)$	$\ln \phi_0(\alpha_{\max})$	Corrected $\ln(\beta/T_{\max}^2)$	$1/T$ (K^{-1})
Analog data							
1.0	4.010	405.0	0.3410	−13.0387	0.13420	−13.1729	1.475*E*−03
2.5	3.460	422.0	0.3680	−12.1720	0.13371	−12.2857	1.439*E*−03
2.5	3.280	421.0	0.3780	−12.1691	0.10567	−12.2748	1.441*E*−03
2.5	3.250	422.0	0.3800	−12.1720	0.10449	−12.2765	1.439*E*−03
5.0	2.790	435.0	0.4090	−11.5159	0.08548	−11.6014	1.412*E*−03
5.0	2.801	435.0	0.4080	−11.5159	0.08598	−11.6019	1.412*E*−03
5.0	2.790	435.0	0.4090	−11.5159	0.08548	−11.6014	1.412*E*−03
10.0	2.752	447.0	0.4110	−10.8563	0.08502	−10.9414	1.389*E*−03
10.0	2.602	448.0	0.4220	−10.8591	0.07811	−10.9372	1.387*E*−03
20.0	2.520	460.0	0.4280	−10.1990	0.07533	−10.2743	1.364*E*−03
20.0	2.790	460.0	0.4080	−10.1990	0.08814	−10.2871	1.364*E*−03
20.0	2.664	460.0	0.4170	−10.1990	0.08218	−10.2811	1.364*E*−03
50.0	2.030	476.0	0.4710	−9.3259	0.05260	−9.3785	1.335*E*−03
50.0	2.010	476.0	0.4730	−9.3259	0.05160	−9.3775	1.335*E*−03
50.0	2.080	476.0	0.4660	−9.3259	0.05508	−9.3809	1.335*E*−03
75.0	1.980	485.0	0.4760	−8.9443	0.05059	−8.9949	1.319*E*−03
75.0	1.930	487.0	0.4810	−8.9495	0.04817	−8.9977	1.316*E*−03
75.0	1.990	486.0	0.4750	−8.9469	0.05115	−8.9981	1.317*E*−03
100.0	1.800	492.0	0.4950	−8.6750	0.04180	−8.7168	1.307*E*−03
100.0	1.762	491.0	0.4990	−8.6724	0.03981	−8.7122	1.309*E*−03
100.0	1.645	490.0	0.5130	−8.6697	0.03376	−8.7035	1.310*E*−03
150.0	1.423	500.0	0.5420	−8.2903	0.02250	−8.3128	1.293*E*−03
150.0	1.440	500.0	0.5400	−8.2903	0.02339	−8.3137	1.293*E*−03

uncorrected: $E = 222.59$ kJ mol^{-1}; $A = 7.376E+15$ min^{-1}; corr. coeff. $= -0.9994$
corrected: $E = 226.98$ kJ mol^{-1}; $A = 1.442E+16$ min^{-1}; corr. coeff. $= -0.9994$

conjunction with eqns. (5a) and (5b). It is pertinent to note that if a regression analysis is performed using the corrected rate data of $\alpha = 0.10–0.65$, i.e., an Arrhenius analysis, according to eqn. (4), one obtains $E = 167.97$ kJ mol^{-1} and $A = 5.157 \times 10^{11}$ min^{-1} with a 0.9900 correlation coefficient. Within the limits of error in calculating the Table 5 input parameters, this is in almost perfect agreement with the Arrhenius analysis data, summarized in Table 2. Simple Friedman plots according to eqn. (5a) are shown in Fig. 6 for fixed extents of reaction from 10 to 70%. The slopes increase with increase in extent of reaction, a fact also reported by Collett and Rand [12] and by Schuker [13]. The Friedman analytical results are summarized in Fig. 7. Although the apparent kinetic parameters, curves A, increase monotonically with extent of reaction, the correct values, curves B, over the limited range, $\alpha = 0.1–0.35$, are essentially constant at $\bar{E} = 264.30$ kJ mol^{-1} and $\bar{A} = 1.712 \times 10^{19}$ min^{-1}. The arrows in Fig. 7 indicate the Kissinger values for E and $\ln A$. The triangles in the BC region of Fig. 5 are the $1 - \alpha$ values calculated using these Friedman kinetic parameters and, as

TABLE 5

Western Kentucky #9, −60 mesh HV B bituminous coal: Friedman analysis parameters, $\beta = 5°\text{C min}^{-1}$, run #1

α	ln(rate)	ln(corrected rate)	$1/T$
0.05	−5.6322E+00	−5.4137E+00	1.6798E−03
0.10	−4.8533E−00	−4.4044E+00	1.5394E−03
0.15	−4.0299E+00	−3.3376E+00	1.4910E−03
0.20	−3.6022E+00	−2.6516E+00	1.4667E−03
0.25	−3.4259E+00	−2.2003E+00	1.4490E−03
0.30	−3.3547E+00	−1.8353E+00	1.4337E−03
0.35	−3.3464E+00	−1.5113E+00	1.4193E−03
0.40	−3.3804E+00	−1.2043E+00	1.4049E−03
0.45	−3.4580E+00	−9.1126E−01	1.3901E−03
0.50	−3.6103E+00	−6.5746E−01	1.3738E−03
0.55	−3.8353E+00	−4.3369E−01	1.3546E−03
0.60	−4.0246E+00	−1.2117E−01	1.3314E−03
0.65	−4.1866E+00	2.8567E−01	1.3053E−03
0.70	−4.7157E+00	4.1325E−01	1.2708E−03
0.75	−4.6796E+00	1.2260E+00	1.2259E−03
0.80	−5.1939E+00	1.6623E+00	1.1750E−03
0.85	−5.3768E+00	2.7050E+00	1.1114E−03
0.90	−5.5195E+00	4.2895E+00	1.0432E−03
0.95	−5.8817E+00	6.8801E+00	9.6341E−04

can be seen, are in very good agreement with those based upon the Kissinger parameters. It has been shown [7] that if extent and rate of reaction data characterizing the behavior of different kinetic models are subjected to Arrhenius analysis assuming an nth order model, widely disparate E and A values result. However, when the same data are subjected to both Kissinger and Friedman analyses, again assuming an nth order model, kinetic parameters close in magnitude to the correct values are obtained. It is considered that such is the case here. The discrepancy between the Arrhenius and Kissinger/Friedman results simply confirms the fact that the assumption of an nth order model to describe the overall process in this region is incorrect.

Region CD may also be subjected to an Arrhenius analysis. It is necessary to employ an nth order model and, furthermore, use the same n value as in region BC. For the data shown in Fig. 5, the kinetic parameters given in Table 2 are obtained, and using them with $n = 4.26$, $1 - \alpha$ values were calculated. The actual and calculated values are so close as to be indistinguishable until point D is reached, when they start to deviate, as shown. Over the heating rate range 1–150°C min^{-1}, the analytical results for this region are fairly consistent, namely, $\bar{E} = 102.79$ kJ mol^{-1} with $\sigma = 3.08$ kJ mol^{-1}, and A varies from ca. 2×10^6 to ca. 6×10^7 min^{-1} as the heating rate varies from 1 to 150°C min^{-1}. The final 15% of the input data, extending over the final 200°C is not amenable to kinetic analysis.

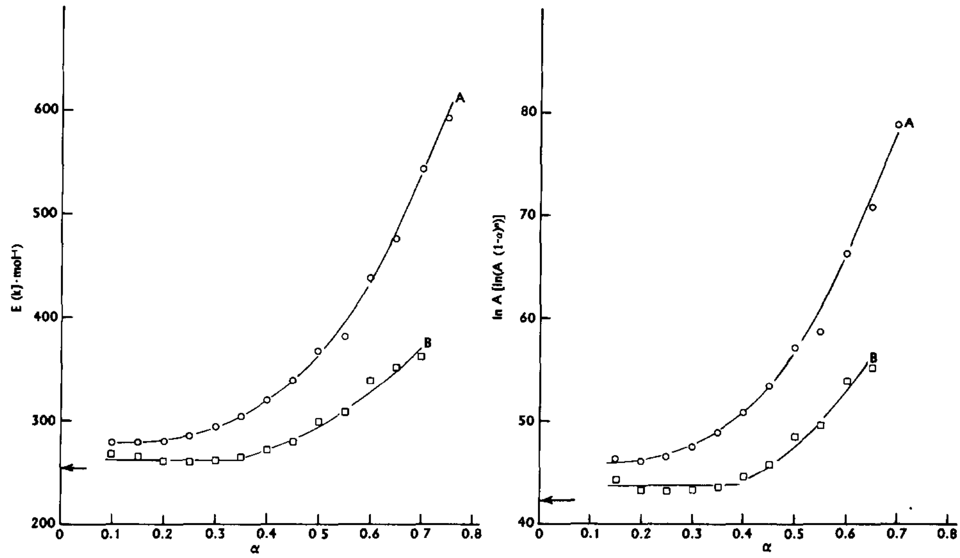

Fig. 7. Western Kentucky #9 high volatile B bituminous coal summary of Friedman analysis kinetic parameter variation with extent of reaction, α. (A) Equation (5a); (B) eqn. (5b).

SUMMARY

The general-purpose program TGKIN has proved highly successful in enabling a complete kinetic analysis of NITG data, transposed into dimensionless extents and rates of reaction as functions of temperature by program TGDATCON.

When used to treat data characterizing the complex pyrolysis of a bituminous coal, it has been shown that the majority of the information can be analyzed by considering it in sections. The boundaries of these regions are defined by performing best-fit Arrhenius analyses. This has proved particularly useful for analyzing the leading and tailing edges of the wide temperature range data. There is every reason to believe that the overall process in the low-temperature region is diffusion-controlled. In the high-temperature region, the multiple processes at work can only be rather nebulously described in terms of the all-encompassing nth order model. However, in both regions, the kinetic parameters, E and A, should be construed solely as empirical parameters. Nevertheless, they do enable an excellent simulation of the input data. In the region of the major weight loss, characterized by the single maximum reaction rate, generalized Kissinger analysis [6] may be used. The resulting kinetic parameters are in very good agreement with those generated from Friedman analyses. The choice of an nth order model to describe this process is based solely on the value of $\alpha_{\max}$ which, or course, is an overall value for a sequence of complex reactions, some mutually independent, some possibly competitive and consecutive. The more correct value of $\alpha_{\max}$ should be based upon the experimental data in the BC region.

However, there is no a priori way by which to define the boundaries of this region before the kinetic analysis. One can only make a guess afterwards.

The coal pyrolysis example is, of course, very complex. However, it does provide data for a complete test of the program. It may be used to investigate the breakdown of less complicated material systems. Thus, it has been employed recently to study the thermal decomposition of calcium carbonate. The results indicate that the solid-state degradation is a diffusion-controlled process with $E = 172.4$ kJ mol^{-1} and $A = 1.97 \times 10^4$ K^{-1} min^{-1}. Details of this work will be the subject of a forthcoming publication [14].

LIST OF SYMBOLS

α	extent of reaction (dimensionless)
$\mathrm{d}\alpha/\mathrm{d}t$	rate of reaction (min^{-1})
$\mathrm{f}(\alpha)$	general expression for kinetic model
$\mathrm{F}(\alpha)$	general expression for the integral of the inverse $\mathrm{f}(\alpha)$ function
T	absolute temperature (K)
E	activation energy (kJ mol^{-1})
A	pre-exponential factor (K^{-m} min^{-1})
m	exponent of weak temperature term in rate equation (1)
R	universal gas constant (8.31434 kJ mol^{-1} K^{-1})
β	heating rate (°C min^{-1} or K min^{-1})
$\mathrm{p}_m(E/RT)$	general function including the exponental temperature integral

ACKNOWLEDGMENTS

This work was conducted as a part of the Kentucky Energy Resource Utilization Program supported by the Commonwealth of Kentucky, Kentucky Energy Cabinet.

The author would like to express his appreciation to Dr. V.B. Reddy for his assistance in testing the program system operation.

REFERENCES

1 J. Zsako and J. Zsako, Jr., J. Therm. Anal., 19 (1980) 333.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 73 (1984) 165.
3 W.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, New York, 1980, Chap. 3, p. 90.
4 J.P. Elder, J. Therm. Anal., 29 (1984) 1327.
5 J.P.Elder, unpublished work.
6 J.P. Elder, in P.S. Gill and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 5, Plenum Press, New York, 1984, p. 269.

7 J.P. Elder, J. Therm. Anal., 30 (1985) 655.
8 J.P. Elder and M.B. Harris, Fuel, 63 (1984) 262.
9 J.P. Elder, Thermochim. Acta, 52 (1982) 235.
10 J.P. Elder, 7th ICTA, Kingston, Ontario, 1982, pap. V-C-5.
11 J.B. Howard, in M.A. Elliott (Ed.), Chemistry of Coal Utilization, Second Supplementary Volume, Wiley-Interscience, New York, 1981, p. 733.
12 G.W. Collett and B. Rand, Thermochim. Acta, 41 (1980) 153.
13 R.C. Schuker, Ind. Eng. Chem., Process Des. Dev., 22 (1983) 615.
14 J.P. Elder and V.B. Reddy, J. Therm. Anal., accepted for publications.