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KINETICS: A Computer Program to Analyze Chemical Reaction Data

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KINETICS: A COMPUTER PROGRAM TO ANALYZE CHEMICAL REACTION DATA

Robert L. Braun and Alan K. Burnham

ABSTRACT

KINETICS (Version 3.2) is a copyrighted, user-friendly kinetics analysis computer program designed for reactions such as kerogen or polymer decomposition. It can fit rate parameters to chemical reaction data (rate or cumulative reacted) measured at a series of constant temperatures, constant heating rates, or arbitrary thermal histories. The program uses two models with conversion-dependent Arrhenius parameters and two models with activation energy distributions. The discrete distribution model fits an average frequency factor and relative fractions and activation energies for up to 25 parallel, first-order reactions. The Gaussian distribution model fits a frequency factor, activation energy, Gaussian distribution parameter, and reaction order for up to 3 parallel reactions. For both distribution models, if the experiments are at a series of constant heating rates, the program uses a very fast approximate fitting procedure to determine possible initial parameter estimates for the subsequent nonlinear regression analysis. This increases the probability that the regression analysis will properly converge with a minimum of computer time. Once convergence is reached by the discrete model, the parameter space is further systematically searched to achieve global convergence. With the Gaussian model, the calculated rates or integrals can be convoluted with an experimental tracer signal during the nonlinear regression to account for dispersion effects often found in real chemical reaction data. KINETICS can also be used in an application mode to calculate reaction rates and integrals for previously determined Gaussian or discrete parameters, using an arbitrary thermal history.

Four additional models have been incorporated for the kinetics analysis of polymers and other materials, including some kerogens, which have a reaction-rate profile that is narrower than that for a single first-order reaction. These include simple 3-parameter and 4-parameter models, a more complex 10-parameter radical-reaction model, and an alternate-pathway model. Convolution of the calculated rates with an experimental tracer during the analysis is also permitted for these methods.

KINETICS is available for PC and UNIX computers and can be run interactively or in a batch mode. An auxiliary program, PLOTKIN, is available to generate a variety of plots from KINETICS output files.

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DEFINITIONS OF FILES

KINETICS.EXE	Executable code for kinetics analysis
PLOTKIN.EXE	Executable code for plotting KINETICS output files
*.DAT	ASCII input file of thermal history and reaction data
*.OUT	ASCII output file of results of the kinetics analysis
*.CON	ASCII input file of controls for running KINETICS in batch mode

KINETICS.EXE and PLOTKIN.EXE should be placed in a directory that is in the PATH command, so that they can be executed from any directory. Approximately 1 Mbyte RAM is required for KINETICS. Using KINETICS on a PC[a] requires that a DOS extender file (DOSXMSF.EXE) be placed in a directory that is in the PATH command. To run KINETICS under WINDOWS further requires that a device driver file (DOSXNT.386) be placed in the

[a] An IBM PC or compatible computer using an 80386 or higher microprocessor with math coprocessor.

WINDOWS directory (*e.g.*, C:\WIN) and the following entry be made in the SYSTEM.INI file under the [386Enh] section: DEVICE=C:\WIN\DOSXNT.386.

Thirty-six characters are allowed for I/O file names, including drive and directory path (on a PC, for example, C:\ROCKEVAL\880929\AP22H25.DAT). Exclusive use of the file extensions .DAT, .OUT, or .CON is not required.

EXECUTION OF KINETICS

KINETICS is executed simply by entering **kinetics**

The following will be displayed at the terminal:

KINETICS Analysis Program: Version 3.2
Robert L. Braun and Alan K. Burnham Lawrence Livermore National Laboratory
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Regents of the University of California

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KINETICS can be run:
1. Using input commands from the keyboard
2. Using input commands from a disk file
3. To prepare a disk file of input commands.

Select desired option [1/2/3]:

KINETICS can be run either by answering questions interactively at the terminal (enter 1) or by using a control file that contains all of the input commands (enter 2). In the latter case, the user is then asked to enter the name of the control file. In either case, the final question after completion of an analysis is whether to begin another analysis. This is especially useful in the batch mode because jobs can be stacked and run unattended. In the interactive mode, the program has additional safety and convenience features. When the output file name is entered, KINETICS checks to see if a file with that name already exists; if so, it asks if the file should be overwritten. When an entered data file name does not exist, it asks again. At any point, the user can back up to the previous question repeatedly by entering no answer to the current question. In the batch mode, an output file will be overwritten if it already exists, and any error in the answer sequence will cause an unpredictable failure of the program. Therefore, we urge extra caution when using the batch mode.

The control file can be made with any text editor if one knows the sequence of input commands needed for the analysis. A more certain way, however, is to have KINETICS prepare

the control file (enter 3). The user is requested to enter the name of the control file. Subsequent answers entered by the user are then recorded in this control file. At the end of preparing the control file, it can be used immediately without reinitializing KINETICS or it can be saved for later use with or without additional editing.

For completely non-interactive use of KINETICS, a previously made control file can be renamed KINETICS.CON. Then, when KINETICS is executed, this control file is automatically used, with no questions asked. This feature is used by the shell program DISCRETE, which asks fewer questions for the commonly used discrete analysis of multiple heating rate data.

Many control files are cited as examples below. These control files and the data files referenced in them are available for tutorial purposes. The first control file that should be used is TEST.CON. This is a relatively fast run, using only 36 data points and 13 discrete energies. The output file, TEST.OUT, can be compared with our output file, OUR-TEST.OUT, to confirm the satisfactory execution of your copy of KINETICS. To automatically run all of the control files, use TESTALL.CON. This requires approximately 30 minutes on a 33 MHz 486DX computer or 10 minutes on a SPARCSTATION-2.

After selecting the desired option in the above menu and entering the name of the control file, if requested, the following is displayed:

Enter title line:
This is any 80-character title or identification line.

Enter output file name:
anyname.out

Kinetic analysis or application methods:

1. Approximate fit using a Gaussian distribution of activation energies.
2. Rigorous fit using a Gaussian distribution of activation energies.
3. Rigorous fit using a discrete distribution of activation energies.
4. Apply Gaussian distribution of activation energies.
5. Apply discrete distribution of activation energies.
6. Narrow-profile fit using 3-parameter model.
7. Narrow-profile fit using 4-parameter Bouster model.
8. Narrow-profile fit using 10-parameter radical-reaction model
9. Alternate pathway fit using $A \rightarrow C$ and $A \rightarrow B \rightarrow C$.

Select desired method [1/2/3/4/5/6/7/8/9]:

Additional information required for the selected method is requested in similar menus. These kinetics analysis or application methods are described in detail later. We have used KINETICS in the analysis of many oil shale, coal, and polymer samples.[1-7]

STRUCTURE OF A DATA FILE

KINETICS can analyze a maximum of 51 data files simultaneously. One data file is usually used for each experiment.[b] File R-25A.DAT is a typical data file for a Rock Eval experiment. The first two lines of each file are reserved for title and identification information. Each line thereafter must contain three entries (space- or comma-delimited, with any mixture of F, E, or I format): time, temperature, and either reaction rate or cumulative amount reacted.

The default unit for time is minutes and the required unit for temperature is degrees Celsius. The time unit may optionally be specified in line 2 of the data file as: time(s), time(m), time(h), time(d), time(y), or time(My), for seconds, minutes, hours, days, years, or millions of years, respectively. Note that the word time must appear and the time unit must follow in parentheses. The time units may be different for each data file.

The rates or cumulative amounts reacted (hereafter the latter is called integral data) may be on a relative scale for each experiment or they may be on an absolute scale (*i.e.*, fraction reacted per second for rate and fraction reacted for integral). Relative data are normalized by the final integral data point, so precautions should be taken to assure that the final point is a representative one and not unduly affected by scatter. A mixture of rate files and cumulative files can be analyzed simultaneously. If one or more files contain absolute data, any relative data files are converted to absolute by assuming that the data extend to complete reaction.

A total of 2000 data points are allowed for the combined data files being analyzed. Analysis time is proportional to the number of points, and we have found that approximately 150 points per experiment are usually adequate. The time entries in each data file must be in ascending order. If KINETICS finds a nonascending time, it issues a warning message and discards that data point. This procedure does not always find the truly invalid data point; therefore, the user should further examine and correct the data file for use in future runs. The data file is read until a blank line or an end-of-file is encountered.

In some experiments, the reaction signal can undergo considerable dispersion before reaching the detector. This can cause serious errors in the data analysis. A tracer signal measured under the same conditions will help quantify the dispersion.[8] To supply tracer data, enter the tracer signal as the fourth entry in each data line. The tracer data can be rate (pulse) or integral (step), but it cannot be a square wave. The tracer data can be on a relative scale and must be supplied for each experiment in the set being analyzed. Use of the tracer data requires that each data file have a constant time step. Blank entries for the tracer rate are permitted once it has decreased to zero. An example of a data file containing a tracer pulse is given in NA-500.DAT. KINETICS permits the use of tracer data only in analysis methods 4, 6, 7, 8, and 9..

The theoretical reaction rates and integrals are determined in KINETICS using the arbitrary thermal history specified by the experimental data. This ordinarily requires that the time and temperature data begin at a negligibly small reaction rate. This requirement is necessary (with one exception, noted later) to initialize the regression analysis for distribution models because the program has to know how to partition the initial fraction reacted among the various parallel reactions. By beginning at a negligibly small reaction rate, the starting integral can be initialized to zero for each energy component in the Gaussian or discrete distribution.

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[b] An exception to this is that a set of experiments with a common thermal history can sometimes be combined into a single data file. For example, the final data points for a set of isothermal hydrous pyrolysis experiments done at the same temperature but for different times can be included in the same file.

This requirement is easily fulfilled by merely extending the thermal history that specifies the actual or estimated sample heatup to an earlier time at which no reaction has taken place. Negative times are acceptable in the data file and are conveniently used in this extension. For a constant heating rate experiment, a single earlier point with a reaction rate or integral of zero will suffice. For a more complex early thermal history (and to supply enough data points to make smooth plots, even for the constant heating rate case) additional points are needed. For each of the extra points, including the very first one, the experimental rate or integral must be entered as -999 to avoid using it in the regression analysis, other than to enable accurate calculation of the rate and integral at the first real data point. This is illustrated in file R-25B.DAT to simulate the case when the rates for the first 30 data points of file R-25A.DAT are assumed to be unknown.

Using one contiguous block of -999 data, starting with the first data point, is the safest way of using this feature. We do allow random mixtures of -999 points with true data points, but the results must be carefully examined for the following two cases: (1) if rate data are interspersed with -999's and then integrated by KINETICS for parameter refinement based on cumulative values and (2) if cumulative data are interspersed with -999's and then differentiated by KINETICS for parameter refinement based on rates. Peculiar results in these cases are sometimes obtained, especially for sparse data sets.

As mentioned above, we allow one exception to the complete thermal history requirement. If the data are on the absolute scale defined above, the first data point may begin at a positive fraction reacted if, and only if, a single Gaussian reaction is being used with the energy distribution parameter constrained to zero. For this case, -999 data must not be used and the calculated integral is initialized to the fraction reacted at the first data point.

INITIAL PROCESSING OF THE DATA FILES

The experimental reaction data are first either numerically integrated by the trapezoidal rule (for rate data) or differentiated by taking central differences (for integral data). By doing this, the subsequent analyses can be done using either rates or integrals or a combination of rates and integrals, regardless of the input data. The program does not consider an unreactive (as distinct from unreacted) fraction. The most common example of this situation is TGA data, where there is usually a residual mass. If the unreactive fraction is independent of heating rate or temperature, there are two ways of treating the data. The unreactive fraction can be subtracted and the data renormalized to give integral data just for the reactive portion. Alternatively, the data analysis can be based on estimated reaction rates, as long as no more than a few percent of the reaction occurs between data points.

A least squares fit of the time-temperature data then determines whether the thermal history is (within imposed tolerances) isothermal, constant heating rate, or arbitrary. The fit is done only over that portion of the data for which the rate is greater than 10% of the maximum rate. For constant nonzero heating rate experiments, the heating rate, Tmax, T50%, and other quantities needed for the approximate Gaussian analysis are determined. Tmax is determined from the rate data by a parabolic least squares fit of the points having rates at or above 90% of the maximum rate. T20%, T50%, and T80% are determined from the integral data by interpolation. If the reaction data are on a relative scale, then the latter three quantities are accurate only if the reaction has progressed to near completion.

For constant heating rate experiments, an asymmetry ratio is also calculated. When rate data are to be used in the kinetic refinement, the asymmetry of the rate profile is the ratio of the

right "half width" to the left "half width" (measured with respect to Tmax) at 10% of the maximum rate. For cumulative data, the asymmetry is (T90% - T50%)/(T50% - T10%).

Several simple kinetic analyses are automatically done, if possible, as a part of the preliminary data reduction. First, if a single data file having a constant heating rate is being analyzed, only a crude analysis can be done to obtain a frequency factor (A) and activation energy (E). No information regarding a distribution of activation energies is obtained. If the reaction does indeed have a significant distribution, the A and E will not be correct.

Second, for two or more data files of any thermal history, a Friedman analysis[9] is done to obtain $\ln[A(1-x)^n]$ and E at fractions reacted of x = 0.1, 0.2, ..., and 0.9. A distribution of activation energies is not obtained, but the presence of a significant distribution can be inferred by a change of E with fraction reacted. In principle, this method can be extended one step further by plotting $\ln[A(1-x)^n]$ vs. $\ln(1-x)$ to obtain n (slope) and A (intercept). KINETICS reports $\ln[A(1-x)^n]$, E, and the values of A for n = 1. For two or more experiments that are done at constant heating rate, a modified Coats-Redfern analysis[10] is also done to obtain a mean A and E for a first-order reaction over the fraction-reacted interval from 0 to 0.1, 0 to 0.2, ..., and 0 to 0.9. Both the Friedman analysis and the modified Coates-Redfern analysis are valid only if the data extend from zero to nearly complete reaction.

Finally, for two or more constant heating rate data files, an approximate Gaussian fit to a first-order reaction is done to obtain an A, E, and S (the Gaussian distribution of E), using improved algorithms[7] similar to those previously reported.[11] The new algorithms are valid for both geological heating rates as low as 0.1 °C/My and laboratory heating rates as high as a few thousand °C/s . This analysis can be based on rates or integrals. Basing it on rates requires a determination of Tmax for at least two experiments and the full width of the reaction rate profile at half height (FWHH) for at least one of those experiments. Similarly, basing it on integrals requires a determination of T50% for at least two experiments and both T20% and T80% for at least one experiment. When analyzing relative integral data, supplied or estimated, the data must extend from zero to near completion of the reaction for the approximate Gaussian analysis method to be accurate, since KINETICS assumes that the final relative integral for each experiment is for the completed reaction. This problem can be avoided by basing the analysis on rates instead of integrals, if the rate data satisfy the criteria just given.

METHOD 1: APPROXIMATE ANALYSIS USING A GAUSSIAN DISTRIBUTION OF ACTIVATION ENERGIES

This option can be used to obtain the approximate Gaussian analysis described in the previous paragraph, if no rigorous Gaussian or discrete analysis is wanted. It requires two or more experiments at constant nonzero heating rates. The required data (heating rate, Tmax, and FWHH for rate analysis, or heating rate, T50%, and T80%-T20% for integral analysis) can be entered from the keyboard or calculated from the detailed data files. Keyboard entry gives only the approximate Gaussian fit, whereas using detailed data files gives the other preliminary analyses, in addition. Files APPROX-A.CON and APPROX-B.CON illustrate the use of input from data files and base the analysis on rates and integrals, respectively. Files APPROX-C.CON and APPROX-D.CON use data entered from the keyboard.

METHOD 2: RIGOROUS ANALYSIS USING A GAUSSIAN DISTRIBUTION OF ACTIVATION ENERGIES

The Gaussian model uses nonlinear regression to simultaneously determine up to 14 parameters: a frequency factor (A), activation energy (E), Gaussian distribution parameter (S), and reaction order (n) for up to three parallel reactions and the fractions (f) reacting by the second and third reaction. An error tolerance of 0.001 is used on all of the scaled parameters: ln(A), E/(10000*R), S, n, and f, where A is expressed in 1/s, E in cal/mol, R in cal/mol_K, and S in %E. The user has independent control over which of the parameters are to be refined. Thus, the model can handle the complex case of multiple parallel reactions as well as the simplest case of a single first-order reaction with no activation energy distribution.

It is important that the initial values of all parameters be very carefully selected to increase the probability of reaching the global minimum in the nonlinear regression. For a single reaction, the parameters are best chosen from the approximate Gaussian fit described above, as illustrated in the file GAUS-A.CON. In this example, A, E, and S are determined by analyzing three data files. The results of the rigorous Gaussian fit are quite close to those obtained by the much faster approximate analysis. When refining S, if its initial estimate is zero, the first trial value in the regression is set to 1. Occasionally smaller values tended to cause the final S to be identical to the initial estimate, whereas with a starting value of 1 it increased or decreased as needed to better fit the data.

Depending on the available data, not all reaction rate parameters can be determined simultaneously. For a single isothermal experiment using the Gaussian model, only A or E and n or S can generally be determined independently. Similarly, for a single experiment at a constant heating rate, the Gaussian model can determine only A, n, and either E or S. Therefore, it is preferable to use at least two experiments. Even for more than two experiments, uniqueness of the rate parameters starts to be a significant problem when more than about 5 parameters are refined.

Fitting two or three reactions requires data over as wide a range of temperatures or heating rates as possible. Even then, unpredictable results are sometimes obtained, since good estimates of the initial parameters are not available from the approximate analyses. Changing the convergence criteria has helped give more meaningful results for some data. Therefore, KINETICS allows two additional options for more than one reaction: (1) using a relative error tolerance that is tighter than the default value of 0.001 and (2) automatically restarting the nonlinear regression to continue the analysis beyond the convergence point until the change in Rnorm (the square root of the sum of the squares of the residuals) between convergences is less than the relative error tolerance. These options may have an effect particularly when there are many local minima in the regression analysis and no multiple reaction model within the specified constraints fits the data very well. Files GAUS-B.CON (without automatic restart) and GAUS-C.CON (with automatic restart) illustrate the differences than can be obtained. We also recommend re-doing the analysis with a different set of initial estimates for the parameters, because of the danger of finding a local minimum that is not the global minimum. The latter risk is not as great when parameters for a single reaction are being refined. However, even then, trying several sets of initial estimates may prove beneficial, particularly in distinguishing between zero and non-zero values of S.

Another useful feature in fitting two or more reactions is the capability of tying together some of the A's during the refinement. KINETICS does this whenever two or more of the initial

values of the A's are equal and are being refined. An example of this is given in GAUS-D.CON. As a warning, do not use the same A as initial guesses unless you want them to be thus constrained.

We have found that dispersion in the experimental data is sometimes important, particularly for isothermal conditions. To help account for dispersion, one can use tracer data to either deconvolute the experimental data or convolute the calculated data. We have found the latter procedure to be the more acceptable one, since it introduces less noise into the results. In the Gaussian model we allow convolution of the calculated rates and integrals with an experimental tracer signal during the regression analysis. An example is given in the file GAUS-E.CON.

METHOD 3: RIGOROUS ANALYSIS USING A DISCRETE DISTRIBUTION OF ACTIVATION ENERGIES

The discrete distribution model fits an average frequency factor and relative fractions and activation energies for up to 25 parallel, first-order reactions. In an outer iterative loop nonlinear regression is used to determine an optimum value of A and in an inner loop constrained linear regression is used to determine the fractions characterized by the various E's for a given value of A. The fractions are constrained to be non-negative and sum to 1. Once convergence of A is reached, the parameter space is further searched by systematically changing A to achieve global convergence. An error tolerance of 0.1 on ln(A) is used during the initial search for the range that probably contains the global minimum and 0.01 is used for the final convergence within that range.

The discrete activation energy model does not have the same limitation as the Gaussian model on how many parameters can be determined (other than the maximum number of 25 fractions fixed by the program's dimensions). However, it has a different problem. Meaningless fractions can be obtained if all of the A-E pairs used in the analysis are not constrained by the data. With constant heating rate experiments, various options are provided for choosing the parameters for the discrete analysis, as shown in the following menu which appears at the completion of the approximate analyses:

Options for choosing the parameters are:

1. User picks fixed E-spacing
2. User picks fixed N-energies
3. User picks initial A-range and fixed E-spacing
4. User picks fixed A-range and fixed E-spacing
5. User picks initial A-range and fixed E-range parameters
6. User picks fixed A-range and fixed E-range parameters

Select desired option [1/2/3/4/5/6]:

For option 1 only the energy spacing is selected; the program selects A, the E-range, and the number of energies (N_e). This is generally the preferred option, since the kinetic parameters are then automatically selected to be within the constraints of the data. For option 2 only N_e is

selected and the program selects the other parameters. While the parameters are again automatically constrained by the data, this is a less useful option because of possible nonintegral energy spacing.

Option 3 is similar to the first option, except the user also picks an A-range to be examined during the first convergence. The final A, however, is permitted to be outside of this range, if that is indicated by the further searching of the parameter space. In option 4 the final A will be within the fixed A-range specified.

For options 5 and 6, the user selects N_e, the E-spacing, the central E, and either an initial A-range to be searched or a fixed A-range. These parameters must be chosen very carefully to avoid spurious results, particularly with the last option. Files DISC-1.CON through DISC-6.CON illustrate each of these options. Note that the frequency factor range specified for the runs using options 3 through 6 purposely excluded the value found with options 1 and 2. Options 3 and 5 still converged on that value, whereas options 4 and 6 did not. Nevertheless, there may be other valid occasions to use the fixed frequency factor range of options 4 and 6.

Occasionally, even with options 1 through 4, a selected activation energy may be slightly out of the range of the data, resulting in a non-trivial fraction at the highest or lowest energy. Because there are usually several local minima with a similar Rnorm, this can cause the principal activation energy to shift slightly from the best value. If a non-trivial fraction is obtained near one of the end energies, the plots should be examined for evidence of an unconstrained reaction. If found, we recommend running the problem again with the parameters chosen manually to eliminate that energy.

The above options are available only when analyzing constant heating rate experiments. Isothermal and arbitrary thermal conditions do not lend themselves well to prescribing A-E pairs that are constrained by the data. Therefore, the user is asked to enter a fixed A-range, N_e, E-spacing, and central E. Because no automatic constraints are used, the results should be carefully examined for spurious behavior. Trying several different parameter sets is recommended. With relative isothermal data, for example, the program sometimes finds a false minimum by ascribing much of the reaction to an A-E pair that is unreactive under the experimental conditions. For that reason, data on an absolute scale are preferred.

In general, two or more constant heating rate experiments are best for the discrete model. We have found cases where the activation energy distributions using the discrete model with a single heating rate were qualitatively correct, but the energies were too high by 5 to 10%. If a given frequency factor is known or desired, the corresponding discrete activation energy distribution can be obtained very rapidly by entering that value for both the minimum and maximum allowed. This last feature may be useful even when there are data at more than one heating rate.

METHODS 4 AND 5: APPLICATION OF GAUSSIAN AND DISCRETE PARAMETERS TO ARBITRARY THERMAL HISTORIES

This option is useful when one has the Gaussian or discrete parameters and wants to follow the net reaction for a given thermal history. The thermal history can be input from either the keyboard or a data file (similar to a normal KINETICS input file, except just the first two entries per data line are needed). In addition to the normally allowed time units, the application mode also allows Mybp (millions of years before present). The reaction parameters can likewise

be obtained from either the keyboard or from a corresponding Gaussian or discrete output file. If KINETICS is used to prepare a control file for this application, reaction parameters that are read from an output file are incorporated into the control file, so that they can readily be modified for later runs. This is a particularly desirable feature for the discrete parameters. If the thermal history is input from keyboard, it is assumed that there is a linear change between each time-temperature pair. Thus, only a few points usually are necessary to define most thermal histories of interest. For plotting purposes, the short keyboard thermal history is expanded to at least 200 points. The calculated rates and integrals are written into a standard output file for plotting. Files APPL-A.CON and APPL-B.CON illustrate the Gaussian and discrete application methods, respectively. For the discrete application method, the residual activation energy distribution is also calculated.

METHODS 6, 7, 8, AND 9: ANALYSIS OF NARROW REACTION RATE PROFILES

Some polymers and other materials have a reaction rate profile that is too narrow to be fit accurately by even a single first-order reaction. If such a fit is attempted, the resulting frequency factor and single activation energy may be excessively high to better accommodate the shape of the profile. Furthermore, these materials may also have a thermal induction period, which can not be simulated by the kinetics analysis methods discussed above. Therefore, we have incorporated four new methods that can address these two aspects. Files NARROW-6.CON, NARROW-7.CON, NARROW-8.CON, AND NARROW-9.CON illustrate the use of these methods in fitting narrow, constant-heating-rate reaction profiles for a material that can not be accurately fit by a single first-order reaction.

Method 6: 3-Parameter Model. The simplest model is $dx/dt = -kx(1-x)^m$, where x = fraction remaining, $k = A\exp(-E/RT)$, and m = exponent. The limit of m = 0 corresponds to a single first-order reaction, while the limit of m = 1 corresponds to the Prout-Thompkins branching nuclei model.[12] The user provides estimated values for A, E, and m, which are then refined by KINETICS.

Method 7: 4-Parameter Model. Another relatively simple model is $dx/dt = -kx(1-x^{2b})^{1/2}$, where $k = A_1\exp(-E_1/RT)$ and $b = A_2\exp(-E_2/RT)$. The user provides estimates for A_1, E_1, A_2, and E_2, which are then further refined. This model is a simplification of the polymer pyrolysis model of Bouster et al.[13]

Method 8: 10-Parameter Radical Reaction Model. Very complex radical reaction schemes using numerous species and reactions have been devised for rigorously simulating chemical reactions[14] and polymer decomposition.[15,16] We have taken a small, but hopefully representative, subset of radical reactions for modeling pyrolysis reactions:

Reaction	Rate Law	Mass Balance
(1) Initiation	$P \rightarrow 2R$	$\Delta P \rightarrow \Delta R$
(2) Recombination/disproportionation	$R + R \rightarrow P + 2E$	$\Delta R \rightarrow \Delta P + \Delta E$

(3) Hydrogen transfer/scission	$R + P \rightarrow 2E + R$	$\Delta P \rightarrow \Delta E$
(4) Volatile product formation	$R + E \rightarrow V + R$	$\Delta E \rightarrow \Delta V$

P = crosslinked polymer, R = radical, E = non-radical end group, V = volatile product.

Eight of the parameters to be refined are the A's and E's for these four reactions. The other two parameters are: F_1 = the ratio of initial E to initial P+E and F_2 = ratio of recombination to recombination + disproportionation for reaction 2. Again, the user must supply estimates for these 10 parameters. For reactions 3 and 4 there are two constraints that can be used. If the initial values of A_3 and A_4 are equal, they are kept equal during the least squares refinement. Similarly, if the initial values of E_3 and E_4 are equal, they are kept equal.

Method 9: Alternate Pathway Model. This model consists of three reactions, (1) $A \rightarrow C$, (2) $A \rightarrow B$, and (3) $B \rightarrow C$. Reactions (1) and (2) are in parallel and reactions (2) and (3) are in series. It is assumed that the data consist of measurements of the final product (C). For analyzing narrow reaction profiles, just the series reactions should be used. This is done by setting A_1 small and/or E_1 large and not refining them. This model is also useful for more general analysis of serial and competing reactions. For the most general model, the A's and E's for all three reactions can be refined simultaneously. Again, initial A's that are equal will be tied together during their least squares refinement.

OUTPUT FILE STRUCTURE

A complete summary of a kinetics analysis or application run is written to the output file specified by the user. In an output file, the reported theoretical rates and integrals are on an absolute scale (*i. e.*, with rates in units of fraction reacted per second and integrals in units of fraction reacted). The reported experimental rates and integrals are also expressed on this scale and, when multiplied by the factor SFACT (given at the start of each data set), they are equal to the input data. For least-squares refinement based on reaction rates, the weighting factor (reported as WTR at the start of each output data set) is the optional user-supplied value divided by the maximum experimental (or estimated) reaction rate on an absolute scale. Thus, if approximately the same number of data points are being analyzed for each experiment, the user need not include any factor to compensate for the inordinately higher weighting which would otherwise be obtained for the higher rate experiments. If the number of data points differs substantially among the various experiments, the user-supplied weighting factor can be used to equalize the weighting. For refinement based on integral data, the weighting factor (WTI) is the user-supplied group weighting factor.

The output file from an application run differs somewhat from the above. The factors SFACT, WTR, and WTI are omitted. In addition, the values in the left column under the heading Rate or Cumulative are the calculated rates or integrals at the time-temperature points supplied from the keyboard, whereas the values in the right column under each heading include interpolated points as well. If the thermal history was input from a data file, then the calculated rates or integrals are only in the right columns.

EXECUTION OF PLOTKIN

The program PLOTKIN (Version 3.2) is available for use on PC or UNIX computers to plot output files from KINETICS, using the public domain graphics library PCDIGLIB (on PC computers) or DIGLIB (on UNIX computers). PLOTKIN is run interactively by entering answers to questions. The user can usually back up to the previous question by entering no answer. An exception to this is the selection of the graphics driver and (on a UNIX computer) the font. To change either of these choices PLOTKIN must be restarted. When one set of plots is finished for a given output file, the option of doing more plots from the same file or from another output file is given.

Plots of rates and/or integrals can be created as a function of temperature or time. In addition, plots of temperature as a function of time are allowed. Although the units of time in the KINETICS output file is seconds, other units (s, m, h, d, y, My, or Mybp) can be specified for the plots in PLOTKIN. The rates in the KINETICS output file are fraction reacted per second, but can be plotted as relative rates by normalizing them by either the calculated or measured maximum rate for each experiment (specified by the user). The integrals are in terms of fraction reacted and are automatically plotted on a 0 to 1 scale. If the output file contains a discrete activation energy distribution, it can also be plotted.

PLOTKIN is executed simply by entering **plotkin**. On a PC, the following menu displays the choice of graphics drivers:

PLOTKIN -- Kinetics Plotting Program: Version 3.2
by Robert L. Braun and Alan K. Burnham, Lawrence Livermore National Laboratory
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Regents of the University of California

Device 1 is CGA Medium Resolution
Device 2 is CGA High Resolution
Device 3 is EGA High Resolution
Device 4 is Postscript Printer Tall
Device 5 is Postscript Printer Long
Device 6 is HP 7475 Plotter Tall
Device 7 is HP 7475 Plotter Long
Number of the graphics device to use?

With option **3** in the above PC menu, the screen can be dumped to a printer by entering **d**. When finished with one plot, press **enter** to receive the next question.

Options **4** and **5** cause an ASCII postscript file named POST.DIG to be written in the current PC directory. The file can then be transferred to the postscript device by the DOS command COPY POST.DIG COM1:, assuming that a postscript printer is connected to COM1 and that COM1 has been configured by MODE COM1:9600,N,8,1,P.

Options **6** and **7** require that the HP plotter be connected to COM1 and that COM1 be configured by MODE COM1:9600,N,8,1. The plotter dip switches must be set at 000101010 for switches S2 through B1, respectively.

REFERENCES

1. Burnham, A. K.; Braun, R. L.; Gregg, H. R.; Samoun, A. M. *Energy & Fuels* **1**, 452-458, 1987.

2. Burnham, A. K.; Braun, R. L.; Samoun, A. M. *Org. Geochem.* **13**, 839-845, 1988.

3. Burnham, A. K.; Braun, R. L., "Kinetics of Polymer Decomposition," Lawrence Livermore National Laboratory Report UCID-21293, 1987, Livermore, CA, Avail. NTIS, Springfield, VA.

4. Burnham, A. K.; Oh, M. S.; Crawford, R., Samoun, A. M. *Energy & Fuels* **3**, 42-55, 1989.

5. Burnham, A. K.; Braun, R. L.; Taylor, R. W.; Coburn, T. T. *Prepr. ACS Div. Petr. Chem.* **34**, 36-42, 1989.

6. Oh, M. S.; Coburn, T. T.; Crawford, R. W.; Burnham, A. K. In Proceedings of the International Conference on Oil Shale and Shale Oil; Zhu Yajie, Ed.; Chemical Industry Press: Beijing, 1988, pp 295-302.

7. Braun, R. L.; Burnham, A. K.; Reynolds, J. G.; Clarkson, J. E. *Energy & Fuels* **5**, 192-204, 1991.

8. Levenspiel, O. *Chemical Reaction Engineering, 2nd Ed.*, Chapter 9, John Wiley & Sons, New York, 1972.

9. Friedman, H. L. *J. Polymer Sci., Part C*, **6**, 183-195, 1963.

10. Coats, A. W.; Redfern, J. P. *Nature* **201**, 68-69, 1964

11. Braun, R. L.; Burnham, A. K. *Energy & Fuels* **1**, 153, 1987.

12. Gadalla, Ahmed M. M. *Thermochimica Acta*, **74**, 255-272, 1984.

13. Bouster, C; Vermande, P; Veron, J. *J. Anal. Appl. Pyrolysis* **1**, 297-313, 1980.

14. Allara, D. L.; Shaw, R. J. *J. Phys. Chem. Ref. Data* **9**, 523, 1980.

15. Jellinek, H. H. G. *Aspects of Degradation and Stabilization of Polymers*, Elsevier, Amsterdam, 1978.

16. David, C. *Chemical Kinetics: Degradation of Polymers*, Volume 14, Chapter 1, Elsevier, Amsterdam, 1978.