

Discrete Distribution of Activation Energies

Reactivity distributions for complex materials are often characterized by distribution of activation energies. The characteristic of a reactivity distribution is that the reaction profile is broader than that of a first-order reaction derived from the shift of any measure of constant conversion versus temperature or heating rate. A diagnostic of inappropriate kinetic analysis common in the published literature is that an apparent low activation energy will be derived from a single heating rate experiment having a broad reaction profile. The Discrete distribution is one of three activation energy distribution models in **Kinetics2015** that is designed to overcome this problem.

The discrete distribution model has its roots in the early German coal literature (Hanbaba P, 1967, and Juntgen and van Heek, 1968). It was subsequently used by Ungerer and Pelet, 1987, to characterize the kinetics of petroleum source rocks, but the first generally practical implementation of the model (PC-based software) was attained by Burnham et al. (1987) in the original version of KINETICS. It is the most widely used reactivity distribution model used for source rock maturity predictions in the petroleum exploration business. Our most complete comparison of this distribution model with other distribution models is given in Burnham and Braun (1999).

The discrete distribution model in **Kinetics2015** fits an average frequency factor and relative fractions and activation energies for up to 500 parallel, first-order reactions with an E-spacing as low as 0.05 kcal/mol. 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 0.001 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 500 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, eight options are provided for choosing the parameters for the discrete analysis:

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
7. User picks fixed A-range and fixed E's: optimize A and fractions
8. User picks fixed A, fixed E's, and fixed fractions
9. Program automatically determines $\ln(A) = a + bE$

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. Even so, spurious contributions at the final energy are sometimes encountered. 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 non-integral energy.

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 (option 5) or a fixed A-range (option 6). These parameters must be chosen very carefully to avoid spurious results, particularly for option 6. If the data do not constrain all components of the specified E-range for the specified fixed A-range, abnormal results for some E's may be obtained.

Options **7** and **8** were added to permit using a set of fixed E's in analyzing data files. In option 7 the fractions at the fixed E's are determined, as A is optimized within the specified A-range. In option 8 all kinetic parameters are fixed. As for option 6, the parameters must be chosen very carefully to avoid spurious results.

Option **9** is new with version 4.2/1.2 and has not been as thoroughly tested as other options. Consequently, it should be used with due caution until more experience has been gained concerning its use.

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.

Options 1 through 5 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. For such conditions, only options 6, 7, or 8 are available. 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.

Occasionally, one wants to know the nature of the sum of squared residuals versus frequency factor in order to judge how accurately it is constrained by the data. The discrete model writes the residual values and frequency factors derived during the course of the refinement to a file with an additional .txt extension. These values can be plotted in a spreadsheet or other program for further assessment.

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