

Kinetics2015: A Computer Program to Analyze Chemical Reaction Data

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Kinetics2015 for Windows XP/Vista/7/8/10 is a copyrighted, user-friendly kinetics analysis computer package designed for reactions such as kerogen, polymer, or mineral 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. In addition to several approximate methods of kinetics analysis, six nonlinear regression methods are available.

Kinetics2015 consists of a DOS kinetics analysis program (Kinetics.exe) and a separate graphic user interface (Kinetics2015EK.exe, version 6xxx). Kinetic analyses can be accomplished by using the graphic user interface (GUI) to set up a control file to run the DOS program. The GUI also contains sections for viewing and editing input data and for plotting output data. The editing and plotting windows have been enhanced significantly over previous versions. The GUI can also be used in an application mode to calculate reaction rates and integrals for previously determined rate parameters for any of the kinetics analysis models, using a constant temperature, a constant heating rate, or an arbitrary thermal history.

A recent feature of **Kinetics2015** is an advanced isoconversional kinetic analysis method, commonly but inappropriately called “model-free” in the thermal analysis community. Our implementation is based on Friedman’s method combined with spline data smoothing to calculate and apparent first-order A and E at each 1% of conversion. The model is now directly connected to the application module.

The nonlinear regression analysis methods range from a single first-order reaction to a variety of activation energy distribution models. The nth-order reaction model can fit activation energy, frequency factor, and reaction order (including $n=1$) for up to three parallel reactions. The nth-order model is equivalent to a Gamma distribution model. The Gaussian activation energy distribution model can fit those three parameters plus a Gaussian distribution parameter for up to three parallel reactions. The Weibull distribution model fits a frequency factor, mean activation energy, a scale parameter related to width, and a distribution shape parameter for up to three parallel reactions. The Discrete-distribution model fits an average frequency factor and relative fractions and activation energies for up to 25 parallel, first-order reactions. One option of the Discrete model allows the frequency factor to increase exponentially with activation energy. The Nucleation-Growth model fits a frequency factor, an activation energy, a nucleation parameter, and a reaction order for up to three parallel reactions. This model is particularly useful for the kinetics analysis of linear polymers, cellulose, and some well-preserved algal kerogens, which have a reaction-rate profile that is narrower than that for a single first-order reaction. A new variation of the Nucleation-Growth model for **Kinetics2015** includes a thermodynamic inhibition term ($1-1/K$), which is particularly useful for deriving phase transition models. Finally, the alternate-pathway model ($A \rightarrow C$, $A \rightarrow B$, and $B \rightarrow C$) can be used for a variety of purposes, including fitting narrow reaction-rate profiles and fitting serial reactions by constraining the $A \rightarrow B$ frequency factor to zero.

When analyzing experiments conducted 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, nth-order, Weibull, nucleation, and alternate-pathway models, 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.