# First and Nth-Order Models

A first-order reaction model is the simplest and most commonly used kinetic model. It starts with the simply statement that the rate of disappearance is proportional to the amount present, $dx/dt = -kx$, where x is the amount remaining and k is a rate constant ordinarily assumed to follow the Arrhenius law, $k = A \exp(-E/RT)$, where A is the frequency factor and E is the activation energy. An nth-order reaction is a simple extension, in which $dx/dt = -kx^n$. Some authors, including ourselves have termed the nth-order reaction, when applied to solid decomposition, as a pseudo-nth-order reaction, because it does not have the classical meaning as a nth-order reaction in the gas phase or solution, in which the reaction rate is proportional to the probability of two reactants bumping into each other. However, more recent theoretical work has shown that the nth-order reaction model is functionally equivalent to having a Gamma distribution of activation energies.

The most common solution to the first-order rate law is the exponential decay for constant temperature. Another common situation is when temperature increases from "zero" at a constant rate, for which a common "exponential of an exponential" approximate solution is often given. Nth-order reactions have analogous non-exponential solutions for these two cases. However, **Kinetics2015** uses neither of those solutions for its nonlinear regression analysis. Instead, the rate is numerically integrated over the time temperature history assuming a constant heating between each time-temperature pair, so it is not constrained to any simple thermal history. A rational approximation of the resulting exponential integral is used (Braun and Burnham, 1987). The model parameters to be refined are determined by minimizing the residual sum of squares between observed and calculated reaction by nonlinear regression. Reaction rates, fractions reacted, or both simultaneously, can be used in the minimization procedure. An error tolerance of 0.001 is used on all of the scaled parameters: $\ln(A)$, $E/(10000*R)$, s, n, and relative fractions for multiple reactions.

Kinetics2015 has the ability of fitting up to three parallel reactions, or up to 11 parameters at once, but in practice, satisfactory convergence is rarely obtained when more than 3 or 4 parameters are refined at once, unless the parallel reactions are well resolved and very good initial guesses are provided. For materials such as calcium oxalate or polyethylmethacrylate that have more than one decomposition peak, it is best to use the T_{max} shift method on both peaks independently, either manually or by splitting the file, to get initial guesses for the A's and E's before analyzing the data as a whole.

One can use the shape and width of the reaction peak at a constant heating rate to determine whether an nth-order reaction is most appropriate. This is seen most easily in the following figure, in which n is varied for constant A and E.
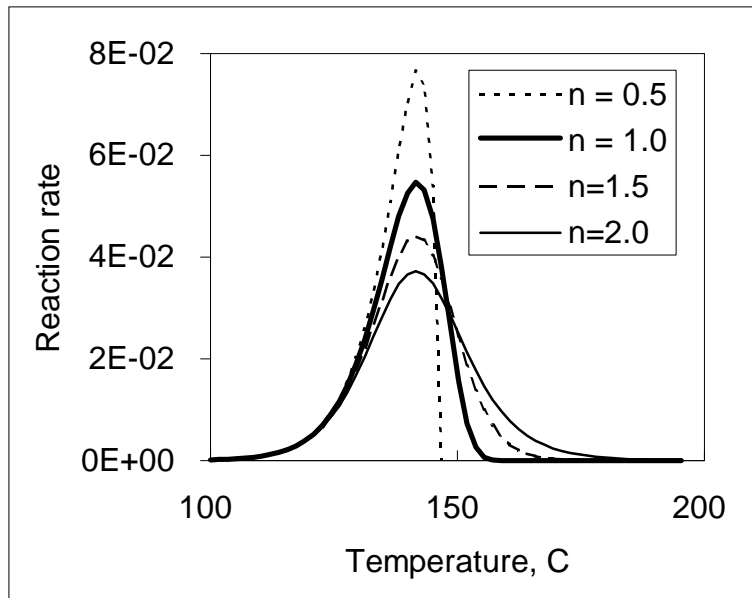
The reaction profile is nearly symmetric for a reaction order of 1.5. For increasing reaction order, the high temperature tail becomes more pronounced. Reaction orders less than one have an increasingly sharp drop after the peak in reaction rate and correspond to shrinking core models. A reaction order of 0.67 corresponds to a shrinking sphere and a reaction order of 0.5 corresponds to a shrinking cylinder. A zero-order reaction represents a constant reaction interface and would increase exponentially until an instantaneous completion of the reaction.

Recent theoretical work (Crickmore, 1989; Boudreau and Ruddick, 1991) has shown that an nth-order reaction is equivalent to a Gamma distribution of reactivity at constant temperature, and it is common to find apparent reaction orders of 3 to 12 in natural systems. The effective reaction order can be a function of temperature, depending on the detailed origin of the underlying reactivity distribution. If one assumes that the reactivity distribution is due to a distribution of activation energies, one can use **Kinetics2015** to calculate the equivalent discrete distribution for a given apparent reaction order of three (with $A = 1 \times 10^{13}$ s^{-1} and $E = 51$ kcal/mol). It is readily apparent that the nth-order reaction is able in three parameters to capture the essence of a very wide activation energy distribution.
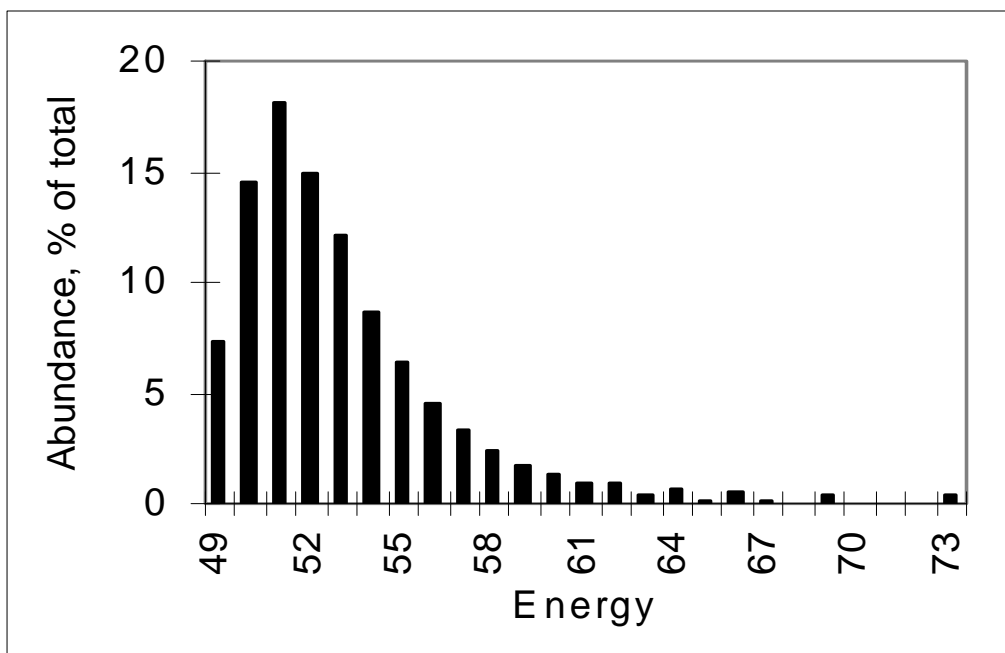
REFERENCES

Braun R. L. and Burnham A. K. (1987) Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models. *Energy & Fuels* **1**, 153-161.

Crickmore P. J. (1989) Power law models as descriptors of the kinetics of complex systems: temperature effects. *Can. J. of Chem. Engr.* **67**, 392-396.

Boudreau B. P. and Ruddick B. R. (1991) On a reactive continuum representation of organic matter diagenesis. *Amer. J. of Science* **291**, 507-538.