## Parallel Nucleation-Growth and Gaussian Model

Some polymers (particularly polyolefins and cellulose), minerals, and kerogens (well-preserved algal) have a reaction rate profile for a constant heating rate that is too narrow to be fit accurately by 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 an acceleratory reaction phase for isothermal conditions, which cannot be simulated by most other kinetics analysis methods.

The classic reaction models in the literature to deal with this type of reaction are the Prout-Tompkins (1944) and Avrami-Erofeev (1939-1961) models. Burnham et al. (1996) compared these two models numerically and found that a simple mathematical extension of the Prout-Tompkins model, which we have called the 3-parameter or narrow profile model, gives a convenient form to fit this type of reaction model. In this case, $dx/dt = -kx(1-0.99x)^m$, where x is the fraction remaining and m is the nucleation exponent. The limit of m = 0 corresponds to a single first-order reaction, while the limit of m = 1 corresponds to the Prout-Tompkins branching nuclei model. The 0.99 coefficient provides an initial nonzero reaction rate and is consistent with the form of Simha's (1956) polymer decomposition model.

Subsequently, we added reaction order as a fitting parameter, giving $dx/dt = -kx^n(1-0.99x)^m$. We call this model the extended Prout-Tompkins model (Burnham and Braun, 1999), although it can also be considered as a special case of the Sestak-Berggren model in which the Avrami parameter, p, is set to zero (Burnham, 2000). Reaction order allows one to change the shape of the profile away from a first-order reaction while maintaining the other characteristics of the nucleation model (i.e., acceleratory phase, narrow profile), as shown in the following plot of normalized rate versus fraction reacted for polystyrene and polyethylene.
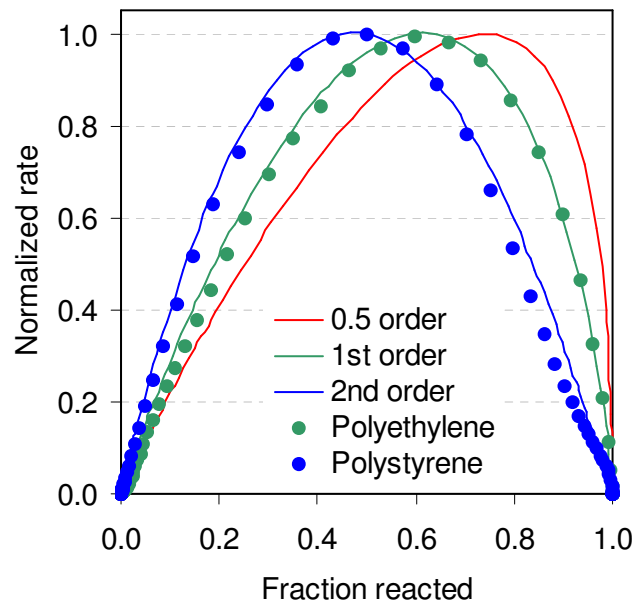
Both materials have a decomposition reaction profile that is narrower than a first-order reaction according to the shift in T_{max}. However, the two materials have significantly different profile shapes: polyethylene has a shape very close to a first-order reaction, while polystyrene is skewed to higher temperature as for a 2nd-order reaction.

The user provides estimated values for A, E, m, and n, which are then refined by **Kinetics2015**. The estimated values can be obtained from the Approximate Analysis for constant heating rate experiments. The Approximate Analysis is printed out only if –0.1<m<1.1. Values outside this rate indicate the model is not applicable. The nth-order nucleation-growth model can fit up to three parallel reactions. In one recent example (Burnham, 2000), the decomposition of ammonium perchlorate (isothermal and constant heating rate) was fitted with two parallel reactions, the first having m=1 and n=1.8 and the second having m=0 and n=0.25.

Nth-order and serial reactions can also be used to model reactions having a narrow reaction profile. While the serial reaction model and the nucleation-growth model are often similar in their ability to fit a data set, the nth-order model has distinctly different characteristics. For a constant heating rate, the nucleation model retains the shape of a first-order model (when reaction rate is plotted versus conversion) as it becomes narrower as m increases. In contrast, the nth-order model becomes increasingly skewed to low temperature as n and the profile width decrease, and it approaches complete reaction with a finite rate. Further, for an isothermal reaction, the nucleation model has an initial acceleratory phase, whereas the maximum reaction rate of the nth-order occurs at initial time.

The extended Prout-Tompkins model is also a special case of an autocatalytic reaction:

$$-dx/dt = k_1 x^{n1} + k_2(x)^{n2}(1-x)^m$$

For $n_1 = n_2 = n$,

$$-dx/dt = k_2 x^n ((1-x)^m + z),$$

where $z = k_1/k_2$. "z" is mathematically similar to the parameter "q". Rearranging the Extended Prout-Tomkins model gives

$$-dx/dt = q^m k x^n [(1-x)+(1-q)/q]^m .$$

Expanding the second term,

$$-dx/dt = q^m k x^n [(1-x)^m + ((1-q)/q)^m + \text{other cross products}]$$

At time zero, 1-x and all cross products are identically zero, so $z = ((1-q)/q)^m$, which is approximately 1-q for q and m close to one. If q is close to one, $(1-x)^m$ becomes larger than the other terms in the brackets as 1-x exceeds 1-q. Equation (4) is normally a good approximation as long as $z \leq 0.04$, and our default value of 1-q is 0.01.

The parameter z (and q by analogy) depends on temperature, but its dependence can be neglected

if z is small or q is close to one and the activation energies of the nucleation and growth reactions are not greatly different. In principle, isothermal experiments could be used to estimate its temperature dependence of q if the induction time does seem to have a markedly different temperature dependence than the overall reaction.
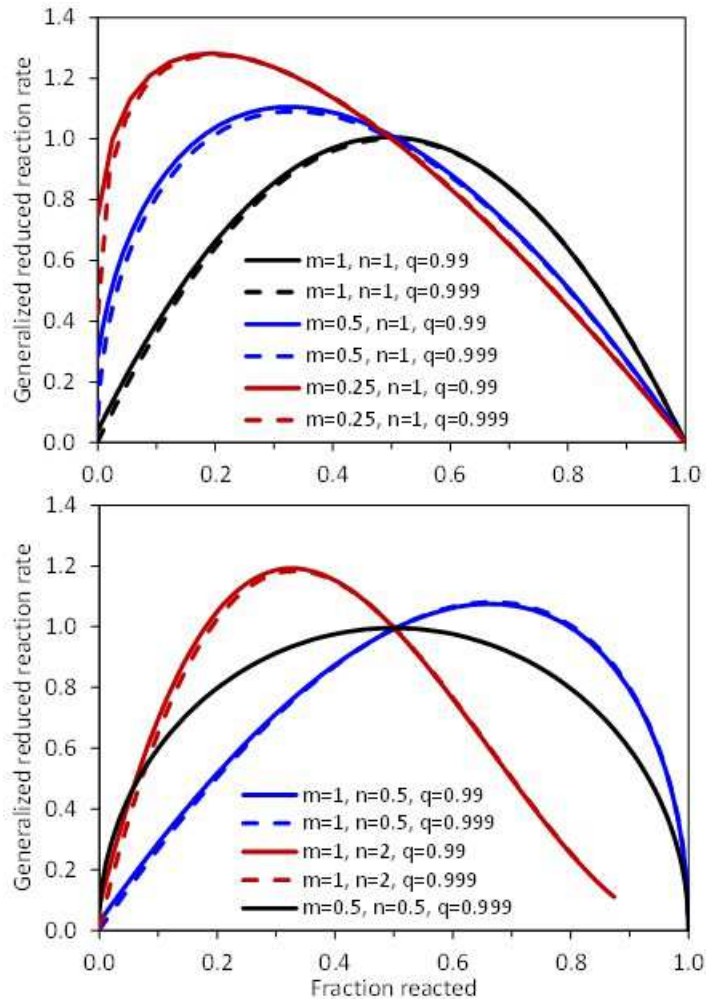
Although q cannot be refined automatically, it can be refined manually. The following figure shows an asymptotic reduction of the residual sum of squares as 1-q approaches zero for a strongly autocatalytic reaction.
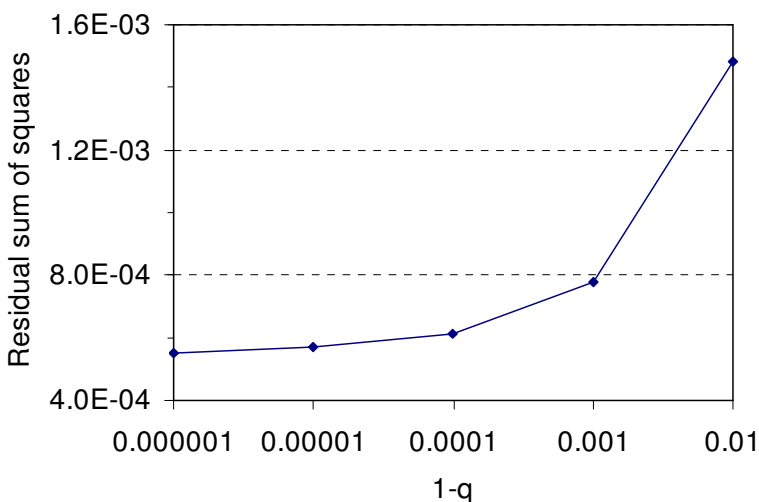
This data set also illustrates that the parameters m and q can compensate for each other.   The variation of m with q, and the resulting estimate of the ratio of the first-order and second-order rate constants (z), is shown in the following table
.

q	m	$z = (1-1/q)^{m}$
0.999999	0.6686	0.000097
0.99999	0.6753	0.00042
0.9999	0.6926	0.0017
0.999	0.7402	0.0060
0.99	0.8983	0.016

More insights into the reaction profile characteristics are available through the Generalized Master Plot feature of **Kinetics2015** described in more detail in the Master Plot help file. The following figure shows how the profile shape changes as a function of the various model parameters. All have an acceleratory phase. The initial rate is determined by the quantity 1-*q*, which is proportional to the ratio of initiation to propagation rates. Plotting the experimental data on this type of plot can help identify an appropriate model and initial guesses for non-linear regression. However, it is equally important to consider the profile width as well as shape. That is particularly easy using the plot generated using the "Model guide" option after the approximate analysis.

Generalized reduced reaction rate

m=1, n=1, q=0.99
m=1, n=1, q=0.999
m=0.5, n=1, q=0.99
m=0.5, n=1, q=0.999
m=0.25, n=1, q=0.99
m=0.25, n=1, q=0.999

m=1, n=0.5, q=0.99
m=1, n=0.5, q=0.999
m=1, n=2, q=0.99
m=1, n=2, q=0.999
m=0.5, n=0.5, q=0.999

Fraction reacted

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