

Approximate Analysis

Kinetics2015 uses several simple calculations to initially determine whether the data are at a constant heating rate and to derive approximate first-order kinetic parameters. The approximate analysis is performed automatically during each new kinetic analysis in order to help derive initial estimates for the subsequent nonlinear regression analyses, which may take several minutes and benefit significantly from good initial guesses.

The reaction rate for an n th-order reaction is given by: $dx/dt = -kx^n$, where x is the fraction remaining and the rate constant k is assumed to have the Arrhenius form, $k = A \exp(-E/RT)$, where A is the frequency factor, and E is the activation energy. When n equals 1, the n th-order reaction simplifies to a first-order reaction, which has a simple exponential solution for constant temperature.

Three basic first-order analyses are available: a Friedman analysis (Friedman, 1963), a modified (i.e., multiple heating rate) Coats-Redfern analysis (Coats and Redfern, 1964, as enhanced by Burnham and Braun, 1999), and a T_{max} -shift method (Kissinger, 1956, 1957). The Friedman analysis works with any thermal history, but the latter two require a constant heating rate. The **Kinetics2015** program first determines whether the time-temperature history is close enough to a constant heating rate before conducted the latter two analyses.

The conventional Friedman analysis assumes an n th-order reaction and is based on an Arrhenius analysis of the instantaneous rates at a specific conversion from each experiment, which hopefully achieve the specified conversion at different temperatures. A plot of $\ln(-dx/dt)$ versus $1/T$ has a slope of $-E/R$ and an intercept $\ln[Ax^n]$. **Kinetics2015** reports A , E , Ax^n , and A for a first-order reaction at 10% conversion levels. The 10% and 90% values are usually unreliable because they are highly sensitive to uncertainties in the data. In principle, a plot of $\ln[Ax^n]$ versus $\ln[x]$ can be used to determine A and n separately, but such plots are rarely linear.

Instead, **Kinetics2015** uses two other methods to estimate A as a function of conversion assuming parallel first-order reactions. The first method (Braun and Burnham, 1987) assumes that the parallel reactions largely overlap and merely substitutes the total fraction reacted and $n = 1$ into Ax^n at each conversion. If the reaction truly is an n th-order reaction with $n > 1$, the calculated frequency factor decreases with conversion. The second method (Hashimoto *et al.*, 1982; Miura, 1995) assumes that the reactions have minimal overlap and only one reaction is important at a specified conversion, so a constant value of $1-x = 0.58$ is used at all conversions, along with the relation $A_{Fr-Miura} = \ln(0.58)H_r E / (RT^2 e^{-E/RT})$.

The modified Coats-Redfern analysis is based on an approximate integrated form of a first-order reaction for a constant heating rate, H_r :

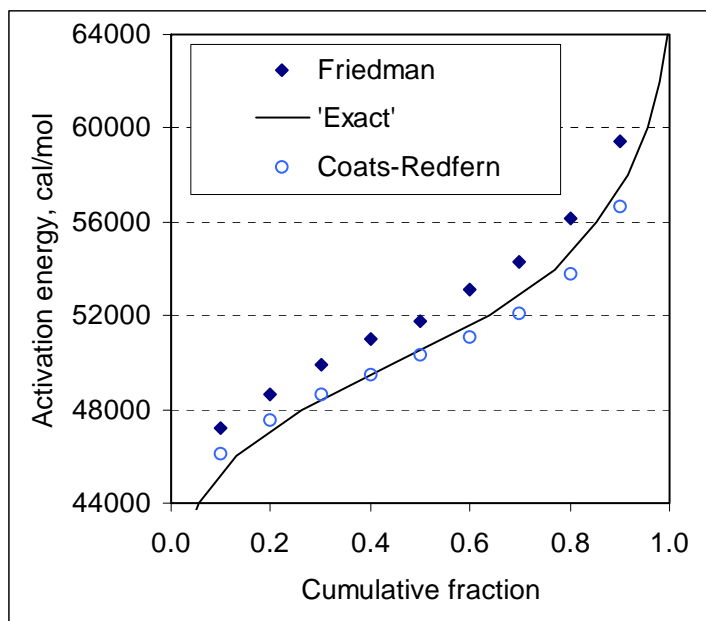
$$\ln[H_r / (T^2(1-2RT/E))] = -E/RT + \ln[-AR / (E \ln(x))].$$

The left side is first plotted versus $-1/T$, assuming $2RT/E = 0$, then E is successively re-substituted into the left-hand side until convergence is obtained, usually in only a few iterations. Since it is a multi-heating rate method, it is actually more similar to the Flynn-Wall-Ozawa method than the original

Coats-Redfern method. Until KINETICS v. 4.05, the coding of this method erroneously used the value of x in place of $1-x$ in one equation, so the reported frequency factors were off by a factor of $\ln(x/(1-x))$. With that error corrected, the frequency factor of this method is similar to that from the Friedman method assuming $n=1$. Alternatively, one can make the same non-overlapping reaction assumption as for the Friedman method and calculate A assuming $1-x = 0.58$ independent of total conversion (Miura, personal communication, 1997).

Both the modified Friedman and Coats-Redfern methods have the ability to check the constant frequency factor assumption used in most activation energy distribution models as well as to determine an approximate energy distribution by differentiating the energy versus conversion curve (Miura, 1995). To check the validity of this approach, we constructed synthetic data at 1 and 10 °C/min for a parallel reaction for which $\ln A$ is a linear function of E . The resulting data were analyzed by the Friedman and Coats-Redfern methods assuming $x =$ total conversion (LLNL) and $1-x = 0.58$ always (Miura).

Both the Friedman and Coats-Redfern analyses recover the cumulative E distribution fairly well, assuming that the conversion plotted is that midway through the reaction having the specified energy. (This cumulative distribution can be numerically differentiated to obtain an energy distribution, but not in the **Kinetics2015** program.)



Superficially, all methods recover the dependence of A on conversion as well. However, when the reaction profiles calculated from the resulting A-E distributions are compared to the original data, differences emerge. In summary, the Friedman method with assuming $n=1$ gets increasingly worse as the distribution increases and is limited to energy distributions with less than 1% standard deviation. The Coats-Redfern parameters calculated with the $n=1$ assumption work somewhat better but are unacceptable for wide energy distributions. In contrast, Miura's approach works well for wide distribution ($\sigma > 5\%$ of E), but it does not work well for narrow distributions. While all these methods are instructive and even accurate for certain limits, they are not generally reliable.

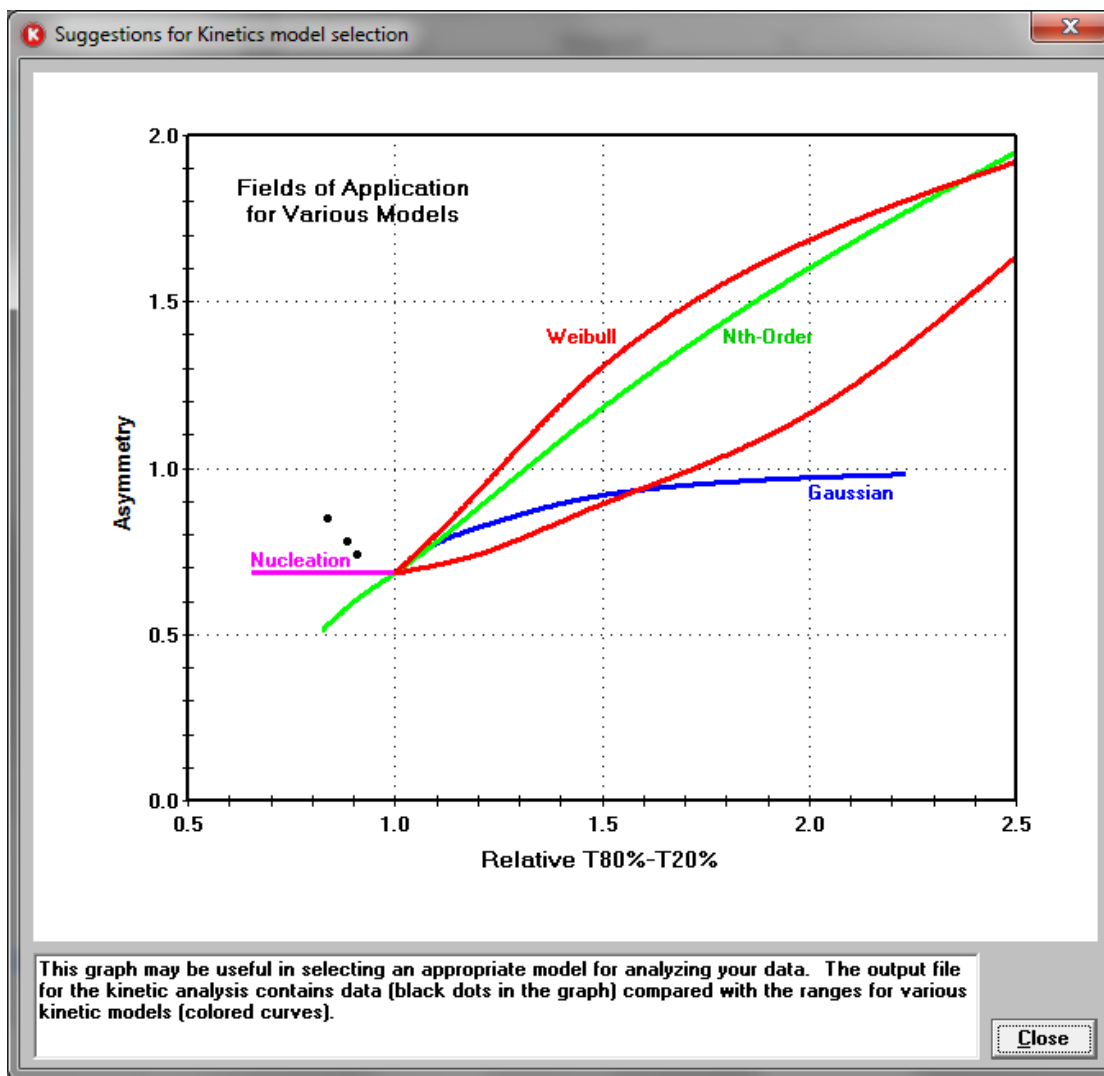
In our experience, the most useful approximate analysis for a constant heating rate is based on the shift of T_{\max} with heating rate:

$$\ln(H_r/T_{\max}^2) = -E/RT_{\max} + \ln(AR/E).$$

This equation is valid for all n th-order reactions (Kissinger, 1956, 1957). The **Kinetics2015** program determines the value of T_{\max} by fitting the top 10% of the reaction profile to a parabola and the value of the heating rate by linear regression of time and temperature over the interval over which the reaction rate exceeds 10% of its peak value.

For constant heating rate data, the width and asymmetry of the reaction profile can be used to estimate parameter values for models other than first-order reactions. The first usage of this technique was by Braun and Burnham (1987), who developed correlations between the Gaussian activation energy distribution parameter, σ , and the relative profile width, i.e., the ratio of the measured profile width to those calculated from the shift in T_{\max} or the 50% conversion temperature. **Kinetics2015** currently uses more accurate correlations reported by Braun et al., 1991. Additional correlations were determined for use with the n th-order, Weibull, and Nucleation-Growth models, and the latter are reported by Burnham (2000). For the nucleation model, the value of A has to be modified from the "Kissinger" value to maintain constant T_{\max} as the nucleation parameter changes.

The values of asymmetry and relative profile width are used to determine which model is most appropriate as well as estimate initial values for the regression analysis. The fields of applicability for the various models are given in a figure brought up by clicking on the "Suggestions" command upon appearance of the approximate kinetic analysis. In the example shown for cellulose pyrolysis, the peaks are slightly narrower than a first-order reaction, which places them in the field of a nucleation-growth model. They are also slightly more symmetric than a first-order reaction, which may indicate a reaction order greater than one. Nonlinear regression analysis found $m = 0.27$ and $n = 1.2$.



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