# Weibull 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 Weibull distribution is one of three activation energy distribution models in **Kinetics2015** that is designed to overcome this problem.

The Weibull distribution was originally derived to model the distribution of mechanical failure strengths (Weibull, 1951). It was first suggested to our knowledge as a distributed chemical reaction law by Burnham et al. (1989) as an alternative to a combination of a Gaussian distribution with an nth-order reaction to account for the breadth and asymmetry of coal pyrolysis profiles. Subsequently, Lakshmanan et al. (1994) explored the use of the Weibull distribution in much greater detail for petroleum source rocks. Our published description of it is in Burnham and Braun (1999).

The introduction of a Weibull distribution follows the formalism of that for the Gaussian distribution of first-order reactions. Again, **Kinetics2015** integrates the rate law over an arbitrary thermal history, and the fraction of material remaining (x) versus time for an arbitrary thermal history is the convolution of the first-order result with the distribution:

$$x = \int_0^\infty \exp\left[-\int_0^t k\,dt\right] D(E)\,dE$$

where for the Weibull distribution,

$$D(E) = (\beta/\eta)[(E-\gamma)/\eta]^{\beta-1} \exp\{-[(E-\gamma)/\eta]^{\beta}\}$$

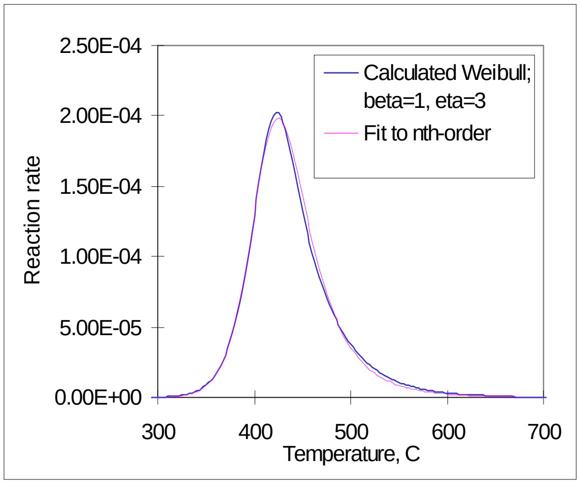
in which $\eta$ is a width parameter, $\beta$ is a shape parameter, and $\gamma$ is the activation energy threshold. In **Kinetics2015**, the fitting parameters are $\beta$, $\gamma$, and the mean activation energy $E_0$, where $E_0$ is defined by

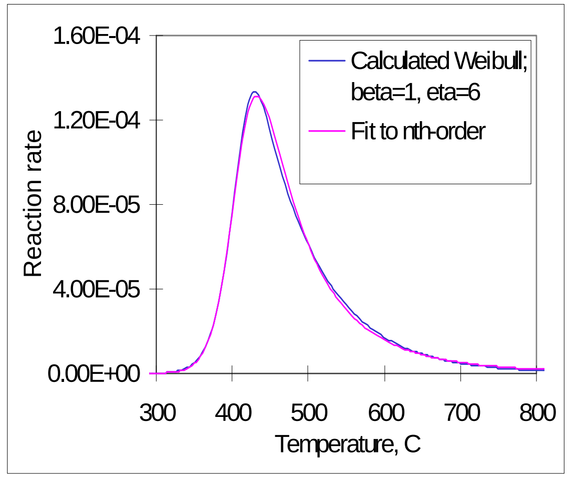
$$E_0 = \gamma + \eta\,\Gamma(1/\beta + 1)$$

$\Gamma$ is the gamma function, and Equation 6.1.35 of Abramowitz and Stegun (1964) is used to evaluate the Gamma function as a function of $\beta$.

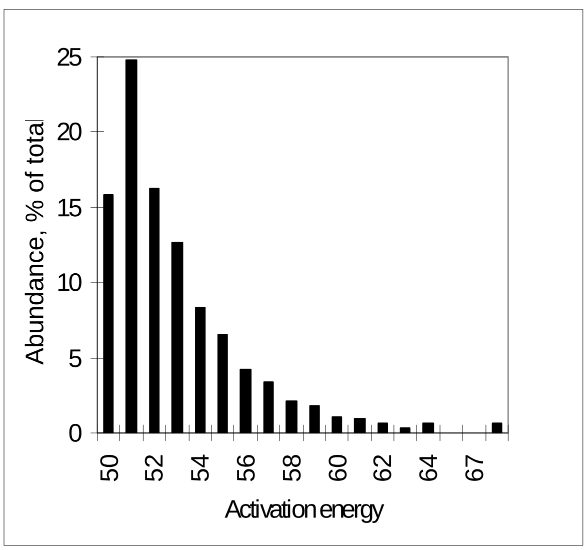
Because the Weibull distribution is less familiar than other approaches, several correlations with other distributions are now given. Nth-order and Weibull distributions with beta equal to one have similar properties. For example, a fit of Weibull distributions with $\beta$ equal to 1 and with $\eta$ equal to 3 and 6 kcal/mol, respectively, to nth-order reactions, yields reaction orders of n=2.7 and n=4.8. The curves differ in detail, but not more than the typical accuracy of experimental data. (All cases presented here used $A = 1\text{x}10^{13}\ s^{-1}$ and $\gamma = 50$

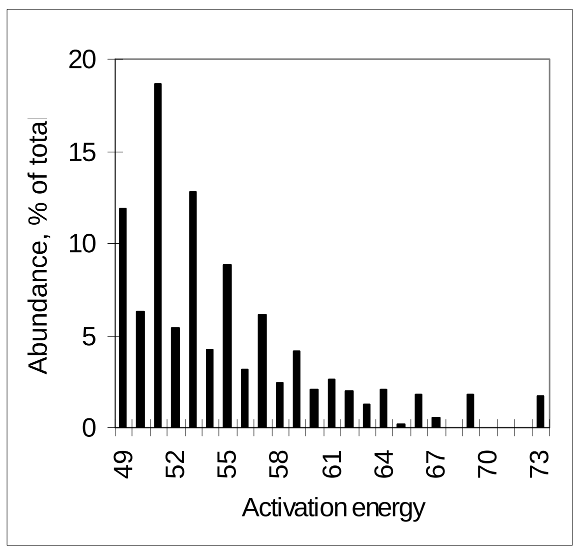
kcal/mol. Synthetic data were created at 1 and 10 K/min and fitted simultaneously, but only 1 K/min results are shown.)



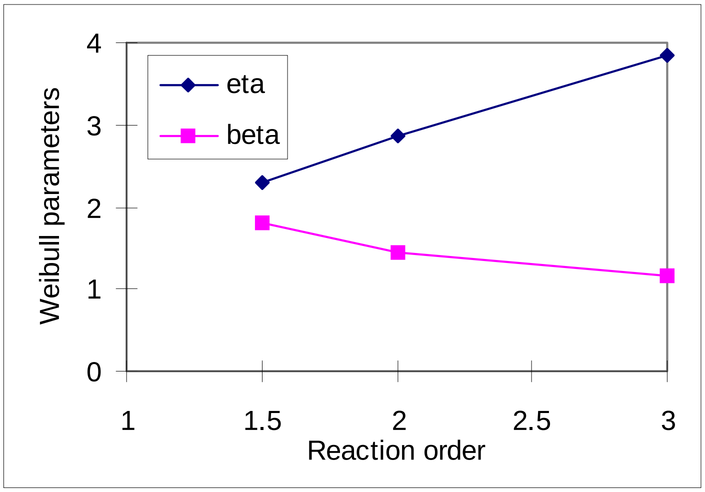




Similarly, synthetic data from Weibull distributions (β=1, η=3 and 6 kcal/mol) were converted to a discrete distributions, as shown in the next figures. The alternating high and low abundances for η equal to 6 kcal/mol is probably a numerical artifact due to the discretization of both the data generation and fitting process.

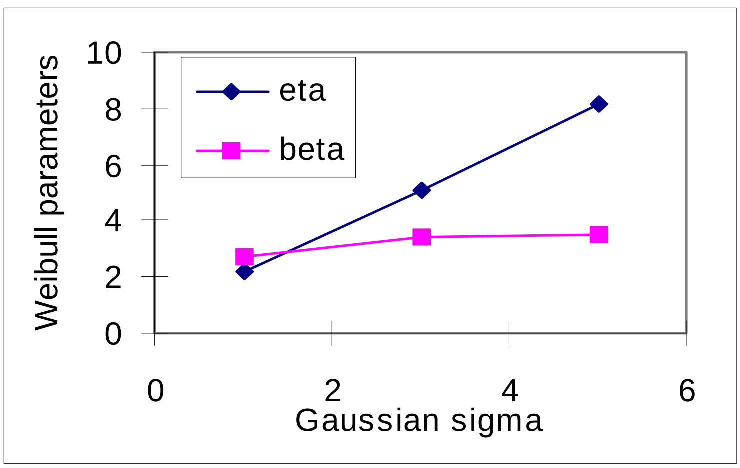



Likewise, other synthetic data from other distributions can be converted to Weibull distributions. Values of ηand β so derived from nth-order reactions of varying reaction order are given in the following figure. For reference, β = 1 corresponds to a simple exponential distribution.




Synthetic data from a Gaussian distribution of activation energies yields a Weibull shape parameter (β) that approaches 3 as the distribution becomes large. For reference, Weibull distributions with β = 5 appear symmetric.

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