

Gaussian Distribution of Activation Energies

Reactivity distributions for complex materials are often characterized by distribution of activation energies. A Gaussian distribution of activation energies is one of the earliest distributions to receive wide usage (Anthony and Howard, 1976, for coal; Campbell et al., 1980, for oil shale; LePoutre, 1981, for petroleum source rocks). Although a distribution in frequency factor is also sometimes considered, the distribution in activation energy is far more common. While one might also expect a distribution in both A and E and perhaps even a correlation in A and E, it is difficult in practice to determine more than a single distribution.

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

The Gaussian distribution model in **Kinetics2015** can consider a distribution of up to three parallel reactions, each being either first-order or nth-order. For a single reaction, the fraction of material remaining (x) versus time for an arbitrary thermal history is:

$$\begin{array}{ll} \text{first-order reaction} & \text{nth-order reaction (n} \neq 1) \\ x = \exp\left[-\int_0^t k \, dt\right] & x = \left[1 - (1-n) \int_0^t k \, dt\right]^{1/(1-n)} \end{array}$$

For a distribution of activation energies, these equations must be integrated over the distributions, giving for first-order and nth-order reactions, respectively:

$$x = \int_0^{\infty} \exp\left[-\int_0^t k \, dt\right] D(E) \, dE \quad x = \int_0^{\infty} \left[1 - (1-n) \int_0^t k \, dt\right]^{1/(1-n)} D(E) \, dE$$

where the integral of D(E) over E itself is unity. For the Gaussian model,

$$D(E) = (2\pi)^{-1/2} \sigma^{-1} \exp[-(E-E_0)^2 / 2\sigma^2]$$

Increasing the Gaussian distribution parameter, σ , makes the reaction profile at a constant heating rate broader and more symmetric. Increasing the reaction order also makes the reaction profile broader and makes it more skewed to high temperature. A combination of n and σ can usually fit a broad reaction profile reasonable well.

While analytical approximations for these and related equations have been made for special circumstances such as a constant heating rate, **Kinetics2015** first breaks up the Gaussian distribution into a number of discrete channels so that the energy between channels does not exceed 0.5 kcal/mol. Each reaction channel is then integrated numerically over the thermal history using a rational approximation of the exponential integral and a linear interpolation of T between each time step (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: $\ln(A)$, $E/(10000 \cdot R)$, S, n, and relative fractions for multiple reactions, where $S = 100\sigma / E_0$.

It is important that the initial values of all parameters be very carefully selected to increase the probability of reaching the global minimum in the nonlinear regression. For a single reaction, the parameters are best chosen from the approximate Gaussian fit. The results of the rigorous Gaussian fit are usually quite close to those obtained by the much faster approximate analysis. When refining S, if its initial estimate is zero, the first trial value in the regression is set to 1. Occasionally smaller values tended to cause the final S to be identical to the initial estimate, whereas with a starting value of 1 it increased or decreased as needed to better fit the data.

While **Kinetics2015** can, in principle, determine A, E, S, n, and the relative fractions of three parallel reactions (14 parameters), it is difficult in practice to reach satisfactory convergence while minimizing more than 3 or 4 parameters. Only one reaction should be used unless there is clear evidence for either a shoulder or distinct reaction peak. Even so, it is sometimes necessary to fix and manually scan a given parameter while minimizing three others in order to obtain reasonable results.

In some cases it necessary to account for the dispersion of the reaction signal between the source and detector. To account for this effect, one can use tracer data (pulse or step function) in the fourth column of the data files. The calculated reaction rates and fractions reacted are first convoluted with the tracer data before comparison to the measurements.

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.
- Anthony D. B. and Howard J. B. (1976) Coal devolatilization and hydrogasification. *AICHE Journal* **22**, 625-656.
- LePoutre (1981) Etude de modelization de la genese des hydrocarbures dans les Bassins Sedimentaires: ENSPM-IFP, as quoted by Ungerer P. (1984) Models of petroleum formation: how to take into account geology and chemical kinetics, in B. Durand (Ed), Thermal Phenomena in Sedimentary Basins, Technip, Paris, p. 235-246.
- Campbell J. H., Koskinas G. J., and Gregg M. (1980) Gas evolution during oil shale pyrolysis. 2. Kinetic analysis. *Fuel* **57**, 377-383.