Equilibrium-Limited Nucleation-Growth Model

Some chemical reactions are close enough to equilibrium that they are affected significantly by back reaction. Particularly common examples are solid-state phase transitions and mineral decomposition reactions in the presence of a non-zero partial pressure of the product gas. Since the back reaction has depends differently on temperature than the forward reaction, the overall apparent activation energy can be a function of temperature. In fact, it can approach infinity close to the equilibrium temperature. Consequently, an activation energy that is too high to be readily explainable in terms of chemical bond strengths may be caused by back reaction characteristics.

The effect of back reaction can be incorporated into the rate expression by including a factor of $(1-1/K_{eq})$—see Bradley (1956), Campbell (1978), and Burnham et al. (2004). At the equilibrium point, this factor equals zero and the reaction stops. The same factor can be used at fixed partial pressure of product gas for mineral decompositions by realizing that one can mimic the full expression $(1-P/K_{eq})$ by changing the pre-exponential factor of the equilibrium constant so it correctly predicts the equilibrium temperature at the partial pressure of interest.

Since the situations we have encountered over the years that need this type of approach also have nucleation-growth characteristics, we implemented it as a modification of the extended Prout-Tompkins model, $dx/dt = -kx^n(1-0.99x)^m$. Those not familiar with it should read the help section for that model and/or Burnham and Braun (1999) and Burnham (2000).

A characteristic of nucleation-growth models is that they depend on the nature of the nucleation sites, which are usually defects. Consequently, a nucleation growth model is not truly reversible along the same path, so the reaction cannot be formulated quantitatively in terms of forward and reverse reactions that operate independent of reaction history and that happen to equal each other at the equilibrium temperature. Instead, we introduce the concept of microreversibility, whereby the reaction in either direction, characterized by the appropriate values of m and n that describe its history, is modified by the equilibrium factor mentioned above. This results in the final equation, $dx/dt = -kx^n(1-0.99x)^m(1-1/K_{eq})$. Only a single reaction is allowed in this implementation.

This model is more sensitive than the others in terms of picking good initial guess to achieve convergence. Often, the entropy and enthalpy of the reaction are known, so the equilibrium parameters can be either fixed or explored manually over small ranges.

An example of the kinds of reaction profiles on might expect are shown in the following figure, which shows the fit of this model to a detailed discrete-particle nucleation-growth model. The equilibrium temperature is 177.5 ^{o}C, and the synthetic data was calculated at 0.1, 1.0, 10, and 100 ^{o}C/min. In this case, the reaction profile is very sharp near the equilibrium temperature at the lowest heating rate and becomes broad at high heating rates because of the lower activation energy for growth than nucleation.

In principle, the reaction model can be used to explore phase transitions during cooling, such as crystallization from the melt, but this application has not been adequately explored to make any judgment on tractability.
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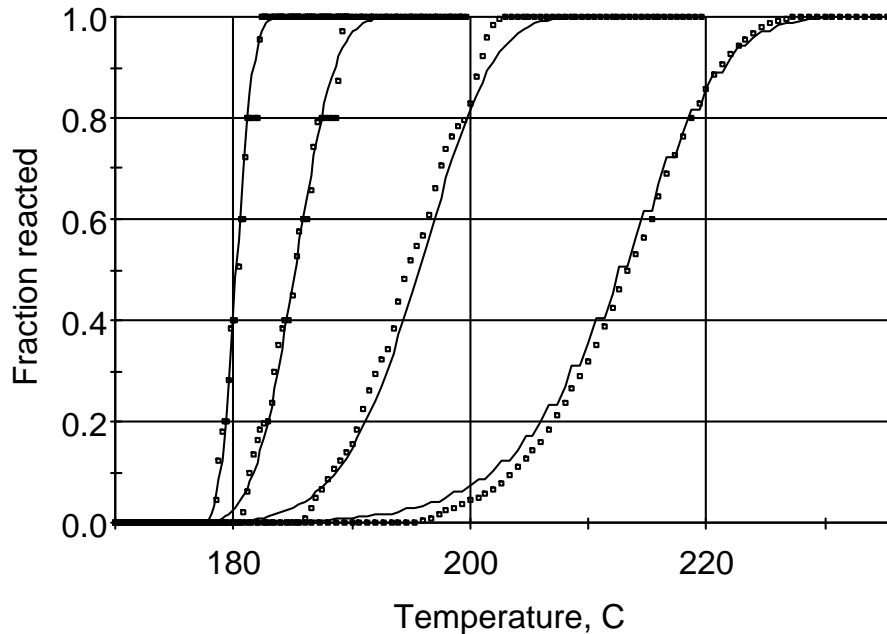
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