

## Sequential Gaussian and Nucleation-Growth Model

Most reactions involve a combination of concurrent and sequential reactions. Other models in **Kinetics2015** have captures many of these possibilities through activation energy distribution, alternate pathway, and nucleation-growth models. However, all these models have certain limitations, and the Sequential Gaussian and Nucleation-Growth model is a more complicated model that includes more detail needed for some applications, but at the expense of not having multiple parallel nucleation-growth models as in the more limited formalism. This is a relatively model that has not been thoroughly tested, so feedback is appreciated.

The model is summarized by the following rate equations

$$dA/dt = -\Sigma k_1 A^{n_1} B^{m_1} \quad (1)$$

$$dB/dt = \Sigma k_1 A^{n_1} B^{m_1} - \Sigma k_2 B^{n_2} - k_3 B^{n_3} C^{m_3} \quad (2)$$

$$dC/dt = \Sigma k_2 B^{n_2} + k_3 B^{n_3} C^{m_3} \quad (3)$$

Reaction (1) is a unique distributed reactivity sigmoidal model. Here,  $\Sigma$  denotes a summation over a distribution of reactions having a Gaussian distribution of energies:

$$D(E) = (2\pi)^{-1/2} \sigma^{-1} \exp[-(E-E_0)^2 / 2\sigma^2] \quad (4)$$

Even though the Gaussian function is a continuous distribution, the implementation involves breaking the reaction into a set of parallel nth-order reactions with an energy spacing not exceeding 0.5 kcal/mol as explained in the Gaussian model description. This reaction does not have a default initiation parameter  $q$  to start the reaction as in our other nucleation-growth model (Burnham and Braun, 1999, and Burnham, 2000). **Therefore, if  $m_1$  is not zero, an initial nonzero value of B must be provided or the reaction will not occur!**

The Sequential Gaussian and Nucleation-Growth Model has several limits:

[1] If  $k_3$  equals zero and  $m_1=0$ , it reduces to the serial reaction model limit of the Alternate Pathway model, except that the Sequential Gaussian and Nucleation-Growth Model can be optimized on any weighted average of B and C. In contrast, the serial reaction limit of the Alternate Pathway model can be optimized only on either B or C separately. In this model,  $k_1$  can be constrained to be equal to  $k_2$  if the initial parameters in the regression analysis are equal.

[2] If  $m_1=0$  and  $k_2=0$ , it reduces to one form of an autocatalytic model, in which there is a distinct reaction intermediate. **This form must have an initial concentration of C for the reaction to proceed past B when  $k_2=0$ .** The initiation reaction (A to B) can be either a distributed reactivity or sigmoidal reaction. An activation energy distribution might represent initiation from a variety of defects with different energies. A sigmoidal reaction might represent sequential steps needed for nucleation.

[3] If  $A=0$  and  $B=1$  at initial time (and  $k_1=0$ ), it reduces to the traditional autocatalytic reaction, which does not require an initial concentration of C, except that our implementation allows the

initiation (or nucleation) reaction to have a reactivity distribution. Again, that could be useful in cases where the initiation comes from a variety of defects with different energies.

[4] The autocatalytic reaction in the preceding paragraph can be further simplified to the Prout-Tompkins limit:

$$-dB/dt = dC/dt = k_3BC = k_3B(1-B) = k_3(1-C)C \quad (5)$$

The issue here is how to get an initial non-zero rate. In the simple Nucleation-Growth (extended Prout-Tompkins) model, we introduced an initiation factor  $q$  plus we also retained the reaction powers to obtain more flexibility in fitting the reaction profile:

$$-dB/dt = k_3 B^n(1-qB)^m \quad (6)$$

An alternate approach to an extended Prout-Tompkins model is to return to the traditional autocatalytic model ( $A=k_1=0$ ), require  $n_2=n_3=n$  and the activation energy distribution of  $k_2$  to be zero, and then factor out  $k_3B^n$ , which gives:

$$dC/dt = k_3 (1-C)^{n3} (C^m + z) \quad (7)$$

where  $z = \Sigma k_2 / k_3$ . If one replaces  $C$  with  $\alpha$ , one gets a form more familiar to the thermal analysis field. To the extent that  $z$  is small and the activation energies of  $k_2$  and  $k_3$  are similar, equation (7) is a good approximation to the full autocatalytic equation. Further manipulation described more fully in the description for the other nucleation-growth model reveals that  $z = ((1-q)/q)^m \approx 1-q$  for  $q$  and  $m \sim 1$ .

## REFERENCES

Burnham A. K. and Braun R. L. (1999) Global Kinetic Analysis of Complex Materials. *Energy & Fuels* **13**, 1-22.

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