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Chemical Engineering Journal 108 (2005) 47–50

Chemical Engineering Journal

www.elsevier.com/locate/cej

Short communication

An *n*th-order Gaussian energy distribution model for sintering

Alan K. Burnham*

Lawrence Livermore National Laboratory, Chemistry and Materials Science, P.O. Box 808, L-282, Livermore, CA 94551, USA

Received 2 September 2004; received in revised form 16 December 2004; accepted 20 December 2004

Abstract

Although it is well known that the rate of sintering is governed by deceleratory kinetics, it is often difficult to fit power-law and *n*th-order reaction models over broad time–temperature ranges. This work shows that a phenomenological model combining a reaction order with an activation energy distribution can correlate surface area as a function of sintering time and temperature over a greater range of those variables. Qualitatively, the activation energy distribution accounts for the dependence of free energy on particle size and material defects, while the reaction order accounts for geometric factors such as a distribution of diffusion lengths. The model is demonstrated for sintering of hydroxyapatite using data of Bailliez and Nzihou [S. Bailliez, A. Nzihou, Chem. Eng. J. 98 (2004) 141–152].

Keywords: Sintering; Kinetics; Activation energy distributions; Modeling; Hydroxyapatite

1. Introduction

Sintering of powders is an industrial practice spanning many applications, and German [1] gives an excellent introduction. In very general terms, sintering is governed by two interrelated properties: a change in free energy, which provides the driving force for the process, and kinetics, which provides the mobility of the system to the lower free energy state. Sintering can occur by many mechanisms, including viscous flow, plastic flow, evaporation–condensation, surface diffusion, volume diffusion, and grain-boundary diffusion.

Predicting the kinetics of sintering has practical aspects for both process optimization and material lifetime prediction. Process optimization is usually easier, because it is usually an interpolation problem for which the calibration data might cover a relatively narrow range of conditions. Lifetime prediction is more challenging, since it involves extrapolation of artificial aging experiments outside the range of calibration. Consequently, a relatively small deviation in a model at the extremes of the calibration data can result in a relatively large error in lifetime prediction if the functional form is not correct.

A vast literature exists on the kinetics of sintering, and various equations have been derived that use powers of time and particle size along with an Arrhenius temperature dependence [1]. However, these models often have difficulty correlating sintering data over wide ranges of time and temperature. For example, the common *n*th-order sintering model often requires *n* to be a function of temperature, with the qualitative justification that the mechanism is changing as a function of temperature (e.g. [2]).

Changes in free energy driving the sintering process are ordinarily attributed to changes in the radius of curvature. Less widely recognized is that sintering often starts with very imperfect crystals that have free energies substantially different from the perfect material. For example, Rogers and Dinegar [3] report that heats of fusion of pentaerythritol tetranitrate (PETN) crystals can have heats of fusion up to 20% less than the single crystal value, and the variation of the heat with crystallization conditions is far greater than with changes in surface area caused by grinding. A free-energy distribution in the starting material will result in an activation energy distribution in the kinetics.

Both *n*th order and activation energy distribution kinetic models have been used extensively for modeling fossil fuel conversion [4–7]. The earliest and simplest energy distribution model used a Gaussian distribution characterized by a

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* Tel.: +1 925 422 7304; fax: +1 925 424 3281.
E-mail address: burnham1@llnl.gov.

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doi:10.1016/j.cej.2004.12.037

mean, E_0, and standard deviation, σ [7]. For systems with modest distributions of reactivity, nth order ($n \leq 2.5$) or Gaussian ($\sigma \leq 3.5\%$ of E_0) models work equally well, even with considerable extrapolation in temperature [8]. However, sintering is often, if not usually, characterized by reaction orders that are considerably larger, and possibly by free-energy distributions as well, if the Rogers and Dinegar result [3] for PETN is typical.

The hypothesis tested in this paper is that the temperature dependence of the reaction order can be removed if the kinetic model also includes an activation energy distribution. We use the data of Bailliez and Nzihou [2], since it covers such a broad range of temperature and degree of sintering. We find that the nth order/Gaussian distribution model works very well, resulting in a reduction in nonlinear-regression residuals compared to the nth-order model typically used for sintering.

2. Sintering models

Deceleratory sintering reactions are often characterized by a power law in time [9,10]

$$\alpha \propto (1 + at)^{-\nu} \tag{1}$$

where α is the extent of reaction (e.g., ratio of the change in surface area to the ultimate change in surface area, or $1 - S/S_0$), a and ν are constants and t the time; or an nth-order reaction [2,11,12],

$$-\mathrm{d}\alpha/\mathrm{d}t \ \propto (1 - \alpha)^n \tag{2}$$

Coming from different fields, Raynaud et al. [13] and Tarutis [14] independently note that the two approaches are actually equivalent, with the exponent of the power law in time being related to the order of the nth-order reaction by $n = 1 + 1/\nu$. Reaction order is commonly interpreted in geometric terms, e.g., shrinking-core reactions are described by $n < 1$ [15]. Tarutis, drawing upon earlier work by Boudreau and Ruddick [16], notes that an nth-order reaction is mathematically equivalent to for $n > 1$ to a Gamma (near-exponential) distribution of reactivity. Consequently, one can consider reaction order as a measure of a distribution of diffusion lengths, for example. Regardless of the precise physical interpretation, n should be constant if the geometric progression of the reaction is independent of temperature, and all temperature dependence would be ascribed to a single activation energy, if one uses the standard Arrhenius rate law.

Alternatively, one can use a Gaussian distribution of activation energies to describe the distribution of reactivity. In this case [17],

$$\mathrm{d}\alpha/\mathrm{d}t = \int_0^\infty k(E) \exp\left[-\int_0^t k(E)\,\mathrm{d}t\right] D(E)\,\mathrm{d}E \qquad \text{(1st order)} \tag{3}$$

and

$$\mathrm{d}\alpha/\mathrm{d}t = \int_0^\infty k(E) \left[1 - (1-n)\int_0^t k(E)\,\mathrm{d}t\right] D(E)\,\mathrm{d}E \qquad (n\text{th order}) \tag{4}$$

where $k = A\exp(-E/RT)$, E is the activation energy, A the frequency factor, R the gas constant, and

$$D(E) = (2\pi)^{-1/2}\sigma^{-1}\exp[-(E - E_0)^2/2\sigma^2] \tag{5}$$

where E_0 is the mean energy and σ the standard deviation. In practice, these equations are implemented in the LLNL kinetics analysis program (Kinetics98 [4], Kinetics2000 [18], and Kinetics05 [19]) by discretizing the distribution into parallel independent 1st- or nth-order reactions having a maximum spacing of 2.1 kJ/mol to cover the required energy interval and then weighting these reactions according to the Gaussian distribution. Each reaction is numerically integrated using the rational approximation to the exponential integral given by Braun and Burnham [17].

Both the simple nth- and 1st-order Gaussian distribution approaches yield deceleratory curves at constant temperature, with the ultimate extent of reaction appearing to depend on temperature when n and σ are large. Calculations for intermediate values of both n and σ are given in Fig. 1. In order to have the overall degree of sintering cover the same range, a higher mean energy is needed for the Gaussian model so

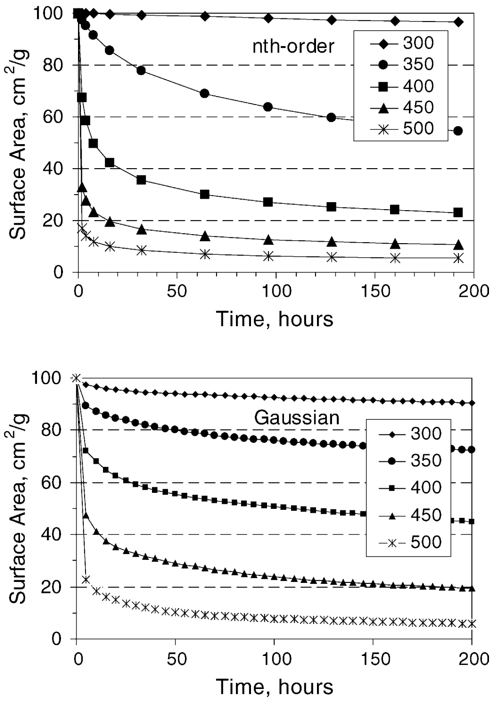

Fig. 1. Idealized sintering curves calculated from nth order (top) and Gaussian activation energy distribution (bottom) models. In both cases, $A = 3 \times 10^{15}\ \mathrm{s}^{-1}$. For the nth-order model, $n = 5$ and $E/R = 30{,}000$ K. For the Gaussian model, $\sigma = 10\%$ of E_0 and $E_0 = 33{,}000$ K. The higher mean energy is needed for the Gaussian model so that the lowest energy channel of the distribution is close to 30,000 K.

that the lowest energy channel of the distribution is close to the single value of the *n*th-order reaction. The shape of the deceleration and how it varies with temperature are different for the two models.

3. Sintering of hydroxyapatite

Bailliez and Nzihou [2] provide an interesting data set for testing the ability of a combined *n*th-order activation energy distribution model to correlate the extent of sintering over a very wide range. They present data for two hydroxyapatites: HAP_{TCP} was formed by reacting $CaCl_2$, H_3PO_4, and NaOH and HAP_{CaO} was formed by reacting $Ca(NO_3)_2$ with $(NH_4)_2HPO_4$ and ammonia. The initial surface areas were 28 and 104 m^2/g, respectively.

Data was digitized from the published plots of surface area versus time at various temperatures. It was then fitted by nonlinear regression to *n*th-order Gaussian, and combined models using the LLNL analysis program Kinetics05. The parameters $\ln(A)$, $E/10{,}000R$, n and σ are optimized to a relative tolerance of 0.001. Results of this analysis are given in Table 1, including a measure of the uncertainties in E, n and σ. A graphical comparison of data with calculation is given in Fig. 2 for the combined model.

When only one of the two parameters (n or σ) is used, a better fit is obtained with the *n*th-order model for HAP_{TCP} and with the Gaussian model for HAP_{CaO}. However, the best fit is obtained for both materials using both model parameters, and it is especially better for HAP_{TCP}. The mean activation energy for the Gaussian model is higher than for the *n*th-order model as explained in the previous section. In work to be reported elsewhere, the energy distribution parameter (σ) is much more important than reaction order (n) for correlating sintering data of the energetic material PETN—negligible improvement in the RSS is obtained by optimizing n in addition to σ, and the optimized value of n is close to unity. This result suggests that using both n and σ for HAP is indeed meaningful.

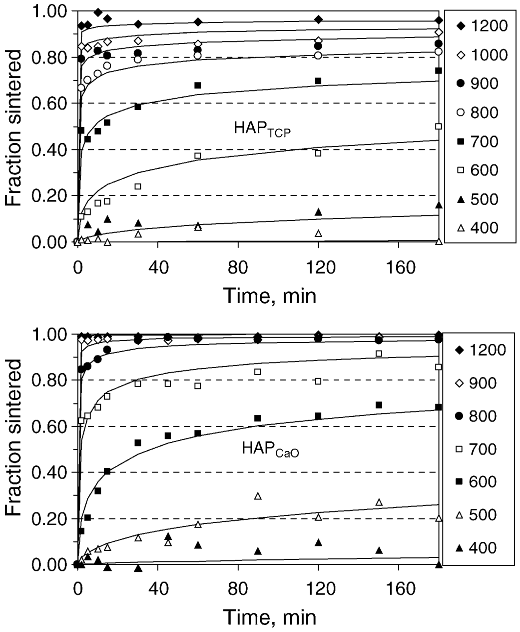

Fig. 2. Comparison of measured and calculated fractions sintered $(1 - S/S_0)$ for the *n*th-order Gaussian energy distribution model. The four model parameters are fitted simultaneously by nonlinear regression and are given in Table 1.

Two related issues are the uncertainties in the parameters and when one should use four rather than three parameters to describe the data. Unlike for linear regression, such questions cannot be answered for nonlinear regression by definitive mathematical formulas. Although linearization methods are commonly used to estimate parameter uncertainties in nonlinear regression, they may be grossly in error unless the model is close to linear [20]. Consequently, the uncertainties reported in Table 1 are those that change the RSS by 10% for the parameter of interest while re-optimizing the other parameters. This difference is large compared to the convergence criteria but comparable to the improvement by using both n and σ instead of the best one of the two. The relative changes in $\ln(A)$ would be similar to those in E/R, since those variables are highly correlated per the well-known compensation law. Of most significance is that the uncertainties in n and σ when both are used are small compared to their values, which supports the conclusion of the previous paragraph.

The activation energies reported here are about one-third lower than those reported by Bailliez and Nzihou [2]. The reason for this discrepancy is not certain, but it may relate to the common problem of deriving activation energies under

Table 1
Hydroxyapatite kinetic parameters derived by nonlinear regression for the Gaussian and *n*th-order reaction models from the data of Bailliez and Nzihou [2]

	A (s^{-1})	E_0/R (K)	n	σ (%) of E_0	RSS[a]
HAP_{TCP}					
*n*th Order (1.1 RSS[b])	8.43×10^{11}	30313 (±7684)	6.89 (±1.56)	0.0	0.1001
Gaussian (1.1 RSS)	1.63×10^{11}	32506 (±16311)	1.00	17.17 (±2.85)	0.3090
Both (1.1 RSS)	1.64×10^{13}	33001 (±7160)	7.01 (±0.32)	6.93 (±1.47)	0.0762
HAP_{CaO}					
*n*th Order (1.1 RSS)	1.79×10^{9}	24246 (±3585)	4.01 (±0.73)	0.0	0.1530
Gaussian (1.1 RSS)	9.44×10^{9}	27383 (±4826)	1.00	11.4 (±1.16)	0.1189
Both (1.1 RSS)	2.92×10^{10}	27149 (±4431)	3.22 (±0.89)	8.32 (±1.40)	0.1046

[a] Residual sum of squares from nonlinear regression.

[b] Change in parameter to increase RSS by 10% while re-optimizing other variables, where indicated.

circumstances where the extent of conversion is not maintained constant. In this case, the activation energy can shift from its true value to make up for other model deficiencies [21]. This is not possible by our method, since the entire data set is fitted simultaneously to the model. Even so, the activation energies are not exceptionally well constrained by the data even in our case, as indicated by the uncertainties given in Table 1.

4. Conclusions

The combination of an *n*th-order reaction model with a Gaussian activation energy distribution provides a simple yet powerful method for correlating sintering data over a very wide time–temperature range. The *n*th-order aspect can be interpreted in terms of standard neck-growth phenomena and a distribution of diffusion lengths. The activation energy distribution reflects the distribution of free energies for imperfect starting crystals. While the combined model fits the data better than either aspect independently for both hydroxyapatite samples examined, the activation energy distribution aspect is considerably more important for the higher surface area material. The activation energies derived by nonlinear regression to the entire range of conversion simultaneously are more reliable than other forms of model fitting that sample different aspects of the reaction at different temperatures.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

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