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NOTATION

A = Antoine constant
B = Antoine constant
C = Antoine constant
p^s = saturated vapor pressure, mm Hg (kPa)
T = temperature, K
x = liquid composition, mole fraction

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Simulation of Pore Growth and Coalescence

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The kinetics of gas-solid reactions are strongly affected by the growth and concomitant overlap of the pores that are the passages by which the gas has access to the reacting solid. Similarly the growth and coalescence of nuclei can play a major role in determining the rate of a solid-phase reaction. The geometric considerations are the same in both cases, differing only in whether the volumes and surfaces of interest are descriptive of filled spaces or voids. In either application, an approach is needed to relate actual changes in geometry to those that would have developed if the pores (or nuclei) had not overlapped. For this purpose Avrami (1940) developed a relationship between actual volume growth and the volume growth of a hypothetical nonoverlapped system:

$$dV = (1 - V)dV_E \tag{1}$$

Since $V \rightarrow 0$ as $V_E \rightarrow 0$, Eq. 1 can be integrated to give

$$V_E = -ln(1 - V) \tag{2}$$

If volume growth is uniform on all surfaces, Bhatia and Perlmutter (1980) have noted that a similar expression relates real and hypothetical surface areas:

$$S = S_E(1 - V) \tag{3}$$

Avrami's formulation has been instrumental in the development of a variety of useful kinetic models for solid phase reactions (Young, 1966; Tompkins, 1976) and for gas-solid systems (Bhatia and Perlmutter, 1980); however, there have been questions raised as to the range of applicability of Avrami's approximation. Noting that Eq. 2 only allows $V = 1$ as $V_E \rightarrow \infty$, Ruckenstein and Vavanellos (1975) and Gavalas (1980) expressed doubts as to whether Avrami's formulation could be precise at high levels of conversion. Bhatia and Perlmutter (1979) had other reservations for the low conversion range over which initial nuclei volumes might be significant but unaccounted for.

In the work reported in this communication, a computer simulation was used to model the growth and coalescence of pores in order to access the accuracy of Avrami's relationships. Following the computational techniques of Mohanty et al. (1982) for evaluating effects of irregular morphology in a porous medium, a sample space of 27,000 cubic building blocks was allowed to represent a reactive sample. The initial porosity was randomly distributed among the cubes, labeling each one as either full or empty. The empty cubes were allowed to grow one block at a time evenly in all directions, and to coalesce with their neighbors where overlap occurred. To keep the sample space representative of an infinite medium, symmetric growth was allowed to enter past a boundary of the space, whenever a cube grew past an opposite boundary. The process was allowed to continue until porosity reached 0.99. The simulation thus produced computed volumes and corresponding surfaces developed at each step of growth on both bases of interest here: 1) as predictions of actual behavior and 2) as hypothetical nonoverlapped configurations. A series of initial porosity values was used, ranging from 0.004 to 0.1. Values less than 0.004 were not used, lest the initial number of empty cubes be insufficient to assure a randomness within the sample space.

The computed results are presented in Figures 1 and 2, using

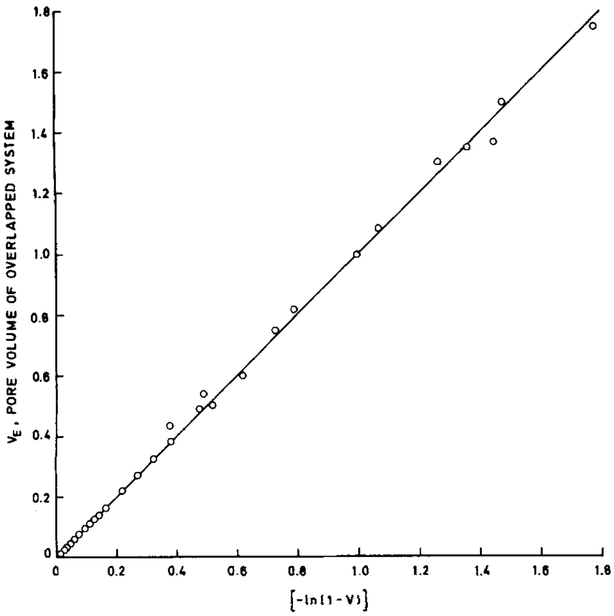

Figure 1. Simulation results for pore volumes of actual and nonoverlapped systems. Straight line is prediction of Eq. 2.

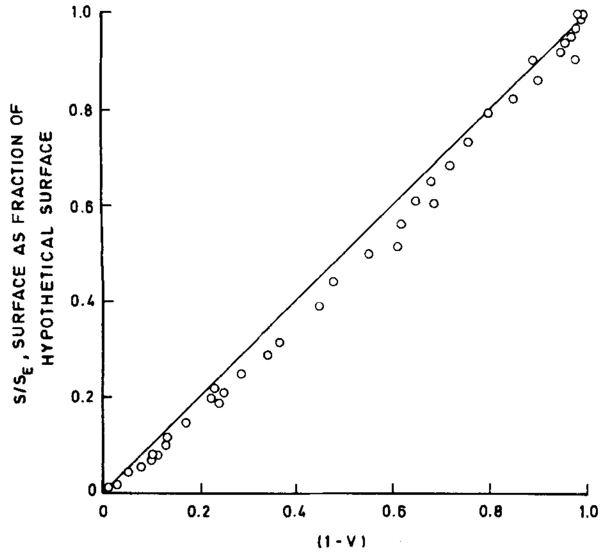

Figure 2. Simulation results for surface areas of actual and nonoverlapped systems. Straight line is prediction of Eq. 3.

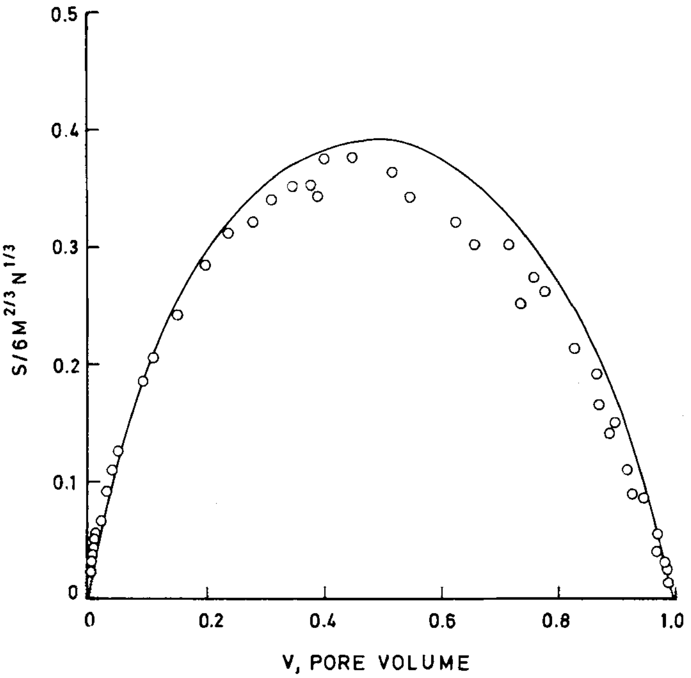

Figure 3. Simulation results for the change of surface area with porosity. Curve is prediction of Eq. 4.

coordinates that would be expected to produce linear correlations with slope of unity if behavior followed the predictions of Eqs. 2 and 3, respectively. The actual pore volumes (allowing for overlap) of Figure 1 are in fact extremely close to the Avrami prediction at least to porosities of 0.85. The simulation results for surface area development give values somewhat smaller than the predictions of Eq. 2, but still within about 15%.

The hypothetical volume and surface terms can be eliminated by combining Eqs. 2 and 3 for a particular geometry to derive an explicit relationship between actual porosity and actual surface area developed. For the system of cubes this leads to

$$\frac{S}{6M^{2/3}N^{1/3}} = (1 - V)[-ln(1 - V)]^{2/3} \qquad (4)$$

where M is the number of building blocks in the sample space, and N is the initial number of empty cubes. Equation 4 predicts a maximum surface area $[S/6M^{2/3}N^{1/3}] = 0.392$ at a porosity $V = 0.49$ regardless of the initial porosity or size of sample space. The maximum occurs when the increase of surface produced by growth is overshadowed by the loss due to pore overlap. A comparison between simulation results and the predictions of Eq. 4 is shown in Figure 3. The simulation results for surface area development are only slightly smaller than the predictions and show the expected maximum between porosities of 0.4 and 0.5. It appears from these findings that Avrami's approximation is of acceptable accuracy for most applications. The computer simulation may also be used to study the evolution of pore (nucleus) size distribution as it results from overlapping, particle disintegration, or nonuniform growth.

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NOTATION

M = number of building blocks in the sample space
N = initial number of empty cubes
S = actual interface surface area of an overlapped system
S_E = hypothetical interface surface area of a nonoverlapped system
V = actual pore volume of an overlapped system per unit volume of space, equivalent to porosity
V_E = hypothetical pore volume of a nonoverlapped system, per unit volume of space

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Two-Equation Model of W. C. Reynolds for Isotropic Turbulence

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In the two-equation model of W. C. Reynolds (1974, 1976) for isotropic turbulence, a closure assumption is made for the rate of change of the isotropic dissipation. We computed in our previous paper the triple velocity correlation function from the Kármán-Howarth equation by using experimentally determined double velocity correlation function and by introducing a parameter that represents the time dependence of the turbulence structure. It is found that our parameter is equivalent to the Reynolds' empirical constant in his closure formulation. We examine here the validity of the Reynolds' formula based on our experimental results.

REYNOLDS' TWO-EQUATION MODEL FOR ISOTROPIC TURBULENCE

The dynamical equations for the turbulence energy q^2 and the isotropic dissipation D can be derived from the Navier-Stokes equations by simple manipulations. For homogeneous isotropic turbulence the equations are reduced to

$$dq^2/dt = -2D, \qquad dD/dt = -W \tag{1}$$

with $q^2 = \overline{u_i u_i}$, $D = \nu\overline{u_{i,j}u_{i,j}}$ and $W = 2\nu\overline{u_{i,j}u_{j,k}u_{k,i}} + 2\nu^2\overline{u_{i,jj}u_{i,kk}}$, where t is the time, ν is the kinematic viscosity, u_i is the fluctuating velocity component, and the subscript after comma denotes partial differentiation with respect to the Cartesian coordinate: $u_{i,j} = \partial u_i/\partial x_j$, $u_{i,jj} = \partial^2 u_i/\partial x_j^2$, etc. On dimensional grounds Reynolds (1974) makes the closure assumption

$$W = c_7 D^2/q^2 \tag{2}$$

to obtain the decay formulae

$$q^2 = q_0^2(1 + t/a)^{-n}, D = D_0(1 + t/a)^{-n-1},$$
$$a = nq_0^2/2D_0, n = 2/(c_7 - 2) \tag{3}$$

where q_0^2 and D_0 are the initial values for $t = 0$.

On the basis of the experimental results of Comte-Bellot and Corrsin (1966) and the suggestion of Lumley and Khajeh-Nouri (1974), Reynolds (1976) proposes $c_7 = 11/3$ for large values of the turbulence Reynolds number $R_\lambda = u'\lambda/\nu$, where u' is the rms value of fluctuating velocity and λ is the lateral microscale defined by

$$\lambda^2 = 5\nu q^2/D \tag{4}$$

In the final period of decay, where R_λ is very small, the inertia terms are unimportant and $c_7 = 14/5$ is valid. Reynolds thus proposes

$$c_7 = \frac{11}{3} - \frac{13}{15}\exp[-(R_\lambda^2/20)^2] \tag{5}$$

EXPERIMENTAL RESULTS OF SATO

In homogenous isotropic turbulence the double and triple velocity correlation functions, $f(r,t)$ and $k(r,t)$, for two points separated by a distance r at time t, are related each other by the Kármán-Howarth equation

$$\frac{\partial}{\partial t}(u'^2 f) = u'^3\frac{1}{r^4}\frac{\partial}{\partial r}(r^4 k) + 2\nu u'^2\frac{1}{r^4}\frac{\partial}{\partial r}\left(r^4\frac{\partial f}{\partial r}\right) \tag{6}$$

Measurements were made by the present authors (Sato 1980; Sato et al., 1983) on the double correlation $f(r,t)$ as a function of $\psi = r/\sqrt{2}\lambda$ and R_λ. In terms of the experimentally determined double correlation function the authors calculated the triple correlation function $k(r,t)$ by equation

$$k(\psi,R_\lambda,I_\lambda) = -\frac{\sqrt{2}}{R_\lambda}\left\{2\psi f + \frac{\partial f}{\partial\psi} + \frac{I_\lambda - 2}{\psi^4}\int_0^\psi \psi^5\frac{\partial f}{\partial\psi}d\psi\right\}$$
$$-\frac{\sqrt{2}\,(5 - I_\lambda)}{\psi^4}\int_0^\psi \psi^4\frac{\partial f}{\partial R_\lambda}d\psi \tag{7}$$

where

$$I_\lambda = (\tfrac{1}{2}\nu)(d\lambda^2/dt) \tag{8}$$

is the parameter representing the time dependence of the turbulence structure. Since $I_\lambda = -5 - (\lambda^2/2\nu D)(dD/dt)$, it would be possible to determine I_λ by direct measurements, but no reliable result has yet been obtained. Consequently, I_λ has been treated as an empirical parameter. By representing the decay of turbulence energy behind a grid of mesh length M in a uniform stream of velocity $\overline{U}$ in the form

$$u'^2/\overline{U}^2 = B_1\xi^{-m}(1 + B_2\xi)^{m-5/2} \tag{9}$$

where $\xi = x/M$ is the nondimensional distance from the grid, and with the aid of the Taylor's hypothesis of the frozen field, the authors obtained