r_i = rate of disappearance for species i
t = time
T = temperature
ΔT = sampling time interval
v = average gas velocity
x = state vector
$\hat{x}$ = state vector estimate
y = measurement vector
z,z' = axial position

Greek Letters

α = catalyst activity coefficient
α_w = overall heat transfer coefficient at the wall
ϵ = porosity of packed bed
λ = heat dispersion coefficient
ρ = mass density
τ = catalyst activity decay time constant
Φ = state transition function

Subscripts

c = catalyst bed
i = discrete spatial location
j = discrete time state
g = gas phase
r = radial component
w = wall
z = axial component

Superscripts

$+$ = *a posteriori* estimate
$-$ = *a priori* estimate

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Modification of Petersen's Model for Porous Solids

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In his pioneering work in the field of kinetics of porous solids, Petersen (1957) introduced the notion that surface area and therefore reaction rate will vary as solid is consumed. The developing surface was modeled as a sum of cylindrical pore contributions reduced by the sum of the effects of the random intersections. The result is a quadratic function of pore radius, which was recast by Szekely et al. (1976) in the form

$$S = 2\pi rL - Kr^2 \qquad (1)$$

Equation 1 predicts

$$S = 0 \quad \text{at} \quad r = 2\pi L/K \qquad (2)$$

Since pore volume is the integral of surface with respect to radius

$$\epsilon = \pi L r^2 - (K/3)r^3 \qquad (3)$$

which has a maximum value of

$$\epsilon = \frac{4}{3}\frac{\pi^3 L^3}{K^2} \quad \text{at} \quad r = 2\pi L/K \qquad (4)$$

By using the initial condition that $\epsilon = \epsilon_0$ at $r = r_0$, Eq. 3 yields

$$\epsilon_0 = \pi L r_0^2 - \left(\frac{K}{3}\right) r_0^3 \qquad (5)$$

Dividing Eq. 3 by 5 gives

$$\frac{\epsilon}{\epsilon_0} = \left(\frac{r}{r_0}\right)^2 \left[\frac{G - (r/r_0)}{G - 1}\right] \qquad (6)$$

where

$$G = 3\pi L/Kr_0 \qquad (7)$$

In order to develop an algorithm for computing G from available initial porosity data, it is useful to evaluate Eq. 6 at $r = (2\pi L/K)$, where

$$\frac{\epsilon}{\epsilon_0} = \frac{4}{27}\frac{G^3}{G-1} \qquad (8)$$

By assuming that $\epsilon = 1$ for this maximum position, Petersen (1957) rearranged Eq. 8 to obtain the cubic relation

$$\frac{4}{27}\epsilon_0 G^3 - G + 1 = 0 \qquad (9)$$

But this assumption is in fact contradicted by Eq. 4. If, instead, the correct value

$$\epsilon = \frac{4}{3}\frac{\pi^3 L^3}{K^2} = \frac{4}{27}\pi L r_0^2 G^2 \qquad (10)$$

is substituted into Eq. 8, one obtains

$$\epsilon_0 = \pi L r_0^2 \left[\frac{G-1}{G}\right] \qquad (11)$$

The identical result could also have been obtained more directly by combining definition 7 with Eq. 5.

DISCUSSION

The essential conclusion to be drawn from Eq. 11 is evident: G depends not only on the initial porosity ϵ_0 but also on the parameter

$$\epsilon_0^* = \pi L r_0^2 \qquad (12)$$

which can be interpreted as a hypothetical initial porosity, the value that would have existed had the pores not had intersections.

From this perspective, Eqs. 11 and 12 combine to give

$$\frac{\epsilon_0}{\epsilon_0^*} = \frac{G-1}{G} \qquad (13)$$

showing the ratio $[(G-1)/G]$ to be the factor that corrects the initial porosity for the effects of pore intersections. It should be noted in passing that the corrected Eqs. 11 and 13 are only valid over a fixed range of the parameter G. To see that this is so, evaluate Eq. 1 for the initial condition:

$$S_0 = 2\pi r_0 L - K r_0^2$$

$$= K r_0^2 \left[\frac{2}{3}G - 1\right] \qquad (14)$$

To assure that the initial pore surface is non-negative:

$$G \geq 3/2 \qquad (15)$$

which implies via Eq. 13 that this model can only be meaningful if

$$\frac{\epsilon_0}{\epsilon_0^*} \geq \frac{1}{3} \qquad (16)$$

Szekely et al. (1976) used Petersen's result to derive a relationship for solid conversion with respect to time. By integrating the reaction rate of the form

$$\frac{dr}{dt} = k_s C^n \qquad (17)$$

they obtained

$$r = r_0 \left(1 + \frac{t}{\tau}\right) \qquad (18)$$

where the dimensionless time is

$$\tau = \frac{k_s C^n}{r_0} \qquad (19)$$

Substitution of Eqs. 6 and 18 into the defining equation for conversion gives

$$X = \frac{\epsilon_0}{(1-\epsilon_0)}\left[\left(1 + \frac{t}{\tau}\right)^2\left(\frac{G - 1 - (t/\tau)}{G-1}\right) - 1\right] \qquad (20)$$

The validity of this result is not affected by the modifications of Petersen's development, provided that the correct value of G is used, computed from Eq. 11 rather than Eq. 9.

A further restriction on Eq. 20 arises from the limited range of validity that must be implicit in Eq. 18, although it was not made explicit in the source cited above. The linear growth of Eq. 18 cannot be consistent with any result that follows from Eq. 1 for any $r > (2\pi L/K)$. This has the effect of limiting the applicability of Eq. 18, and therefore Eq. 20, to

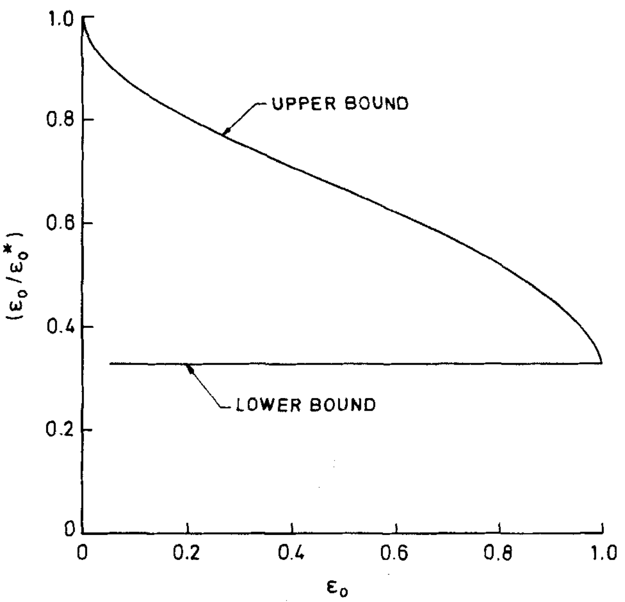

Figure 1. Bounds on $(\epsilon_0/\epsilon_0^*)$ for given initial porosities.

$$\frac{t}{\tau} \leq \frac{2}{3}G - 1 \qquad (21)$$

With this restriction, Eq. 20 yields

$$X \leq \frac{\epsilon_0}{1-\epsilon_0}\left[\frac{4}{27}\frac{G^3}{(G-1)} - 1\right] \qquad (22)$$

Comparison of this result with Eq. 9 leads to the conclusion that the former equation would force complete conversion ($X = 1$) as the only possible solution, clearly an unacceptable formulation. Equation 9 can, however, be resurrected as an inequality to provide an upper bound on values of G that are permitted, since $X \leq 1$ requires

$$\frac{4}{27}\epsilon_0 G^3 - G + 1 \geq 0 \qquad (23)$$

Each value of initial porosity ϵ_0 corresponds to a limiting G, which in turn produces an upper bound on $(\epsilon_0/\epsilon_0^*)$ via Eq. 13. Numerical results of such computations are presented in Figure 1, together with the lower bound Eq. 16. Taken in combination these bounds leave a rather restrictive region of model applicability at even moderate porosity levels. For $\epsilon_0 = 0.5$, for example

$$1.5 < G < 3.0$$

$$0.33 < (\epsilon_0/\epsilon_0^*) < 0.67$$

The value of L and r_0 that are called for in Eqs. 11 and 12 are both fixed by the initial pore structure of the solid reactant and can therefore in principle be determined experimentally before the reaction has begun. If, for example, porosimetry is used to measure the distribution of pore volume as a function of pore radius, the total pore length can be computed by

$$L = \frac{1}{\pi}\int_0^{\infty}\frac{1}{r^2}v(r)dr \qquad (18)$$

where, however, it should be noted that although cylindrical pore geometry is implied, no provision is made for pore intersections. Indeed, this is an important shortcoming of the Petersen model, for there is no experiment available to measure L exactly.

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NOTATION

C = concentration of gas reactant
G = $3\,\pi L/Kr_0$
k_s = kinetic rate constant
K = constant defined by Eq. 1
L = total pore length
n = order of reaction
r = pore radius
r_0 = initial pore radius
S = surface area
S_0 = initial surface area
t = time
v = pore volume distribution function
X = conversion

Greek Letters

ϵ = porosity
ϵ_0 = initial porosity
ϵ_0^* = πr_0^2

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