An Effectiveness Factor Approximation for Pore Size Distributions

KENJI HASHIMOTO and P. L. SILVESTON

University of Waterloo, Waterloo, Ontario, Canada

Mingle and Smith (*1*) considered the effect of pore size distribution on the micropore effectiveness factor. Their results suggest that, for a first-order irreversible reaction catalyzed by the solid, a satisfactory approximation is

$$E = \frac{\tanh h_e}{h_e} \qquad (1)$$

where h_e is the Thiele modulus based upon r_e, the effective pore radius of Wheeler (*2*). This useful approximation may be obtained in a more rigorous manner by the use of the mean value theorem of integrals. Our purpose here is to derive Equation (1) by this theorem and thereby introduce a technique for generating approximations for functions like effectiveness factors in cases where pore size distributions must be considered.

For an irreversible reaction following the mass action law, the concept of an effectiveness factor leads to

$$E = \frac{\int_0^\infty \pi r^2 \left(- D_e \frac{\delta C}{\delta z}\bigg|_0 \right) f(r) dr}{\int_0^\infty 2\pi r\, \bar{l}\, k_n C_0^n f(r) dr} \qquad (2)$$

assuming cylindrically shaped pores of radius r and mean length $\bar{l}$. $f(r)$ is the probability density function, such that $f(r)dr$ is the number of open pores having a radius between r and $r + dr$ per unit volume of the solid. Restricting discussion to an isothermal, first-order, irreversible reaction, solving for the concentration gradient and introducing a dimensionless radius ρ, a dimensionless effective diffusivity $\mathfrak{D}$, and the Thiele modulus $h_0 = \bar{l}\sqrt{\frac{2k_1}{r_0 D_{e0}}}$, where r_0 is the most probable or mean radius defined by the first and zeroth moments of the $f(r)$ distribution and D_{e0} is the effective diffusivity evaluated at r_0:

$$E = \frac{1}{h_0} \frac{\int_0^\infty \rho^{3/2} \mathfrak{D}^{1/2} \tanh\left(\frac{h_0}{\sqrt{\rho \mathfrak{D}}} \right) f(\rho) d\rho}{\int_0^\infty \rho f(\rho) d\rho} \qquad (3)$$

If only Knudsen diffusion occurs in the pores, Equation (3) becomes

$$E_k = \frac{1}{h_0} \frac{\int_0^\infty \rho^2 \tanh\left(\frac{h_0}{\rho} \right) f(\rho) d\rho}{\int_0^\infty \rho f(\rho) d\rho} \qquad (4)$$

since $\mathfrak{D} = \rho$. Equation (4) is the simplest form Equation (2) takes. Unfortunately, an analytical form seems possible only in the case of a uniform pore size distribution.

According to the mean value theorem for integrals (*3*), there exists a value of x^* of x in (a, b) such that

$$\int_a^b y(x)\, g(x) dx = y(x^*) \int_a^b g(x) dx \qquad (5)$$

provided $g(x)$ is of constant sign in the interval. Applying this theorem to Equation (4)

$$E_k = \frac{m_2}{h_0 m_1} \tanh\left(\frac{h_0}{\rho_k^*} \right) \qquad (6)$$

where m_n is the nth moment of the $f(\rho)$ distribution. ρ_k^* is the value of ρ which satisfies the theorem [Equation (5)] or an approximation. The approximation may be found by requiring that the asymptotes of Equation (6) with respect to h_0 must be the same as those for Equation (4). These are $E_k = 1$, if $h_0 \to 0$ and $E_k = m_2/h_0 m_1$ as $h_0 \to \infty$. Consequently, $\rho_k^* = m_2/m_1$ must be the approximation for the Knudsen diffusion case, or

$$E_k = \frac{\tanh\left(\frac{m_1 h_0}{m_2} \right)}{\frac{m_1 h_0}{m_2}} \qquad (7)$$

For cylindrical pores, Equation (7) reduces to Equation (1) since

$$\frac{m_2}{m_1} = \frac{2\, V_g}{r_0\, S_g} = \frac{r_e}{r_0} \qquad (8)$$

and D_{e0} is the Knudsen diffusivity which is directly proportional to r_0.

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NOTATION

C, C_0 = reactant concentration in pore, at pore mouth
D_e, D_{e0}, D_{ee} = effective diffusivity, for $r = r_0$, for $r = r_e$
$\mathfrak{D}$ = dimensionless effective diffusivity = D_e/D_{e0}
E, E_k = effectiveness factor, with Knudsen diffusion
f = probability density function of pore size
h_0 = Thiele modulus based on most probable pore radius = $\bar{l}\sqrt{\frac{2k_1}{r_0 D_{e0}}}$
h_e = Thiele modulus based on effective pore radius = $\bar{l}\sqrt{\frac{2k_1}{r_e D_{ee}}}$
k_n = reaction rate constant for order n reaction based on surface area
$\bar{l}$ = mean pore length
m_n = nth moment of $f(\rho)$
r, r_0 = pore radius, most probable pore radius
r_e = mean pore radius = $2\, V_g/S_g$
S_g = total surface area, usually micropore surface area/g. of solid
V_g = total pore volume, usually micropore volume/g. of solid
ρ = dimensionless pore radius = r/r_0

LITERATURE CITED

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Kenji Hashimoto is at Kyoto University, Kyoto, Japan.