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NUMERICAL CALCULATIONS FOR THE ASYMPTOTIC, DIFFUSION DOMINATED MASS-TRANSFER COEFFICIENT IN PACKED BED REACTORS

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Numerical Calculations for the Asymptotic, Diffusion Dominated Mass-Transfer Coefficient in Packed Bed Reactors

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Abstract

For deep beds, the effective Sherwood number approaches a proportional relationship to the Péclet number as the Péclet number tends to zero. A sinusoidal periodically constricted tube model for the voids in the bed has been used to predict the constant of proportionality. This constant depends upon the dimensionless ratios of three lengths: the average tube radius, the oscillation amplitude, and wavelength.

Work performed under the auspices of the U. S. Department of Energy.

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In an earlier publication (1) we have presented a formal method for calculating the Sherwood number in the low Péclet number regime for a mass-transfer limited, packed bed reactor. Emphasis was placed on the important distinction at low Péclet numbers between the effective Sherwood number, which relates the inlet and outlet concentrations, and the film Sherwood number, which is a sink term in the one dimensional model of the bed. A singular perturbation solution for the concentration field was used to demonstrate that to first order in deep beds, the effective Sherwood number can be written

$$\frac{\varepsilon k_m}{a\mathcal{D}_o} = \frac{v}{a\mathcal{D}_o}\left(\alpha_1 - \frac{\varepsilon}{aL}\ln\frac{v}{\alpha_2 a\mathcal{D}_o}\right) \tag{1}$$

where α_1 and α_2 are constants which depend only upon the bed structure and are independent of the Péclet number. Equation 1 applies for any detailed void volume arrangement of the bed.

In order to introduce a predictive capability to the formalism presented in that work, a microscopic model for the solid-void structure of the bed must be introduced. In this note, we present values of α_1 calculated using the periodically constricted tube (PCT) model of the bed. In order to avoid repetition, we shall assume familiarity with our earlier publication (1).

Periodically Constricted Tube Model

The voids in a bed of nonconsolidated porous media can be modeled as an array of periodically constricted tubes. This concept

has been developed by Payatakes et al. (4) and the references therein. In this work, the bed is modeled as an array of sinusoidal PCT (figure 1). We have previously exploited this particular geometry to calculate the high Péclet number, deep bed Sherwood number (2).

The first order solution for the concentration variable in the reactive section of the bed has been shown to be governed by Laplace's equation. The concentration variable within the model microscopic void volume will thus satisfy Laplace's equation.

$$\frac{\partial^2\bar{\theta}}{\partial z^2} + \frac{\partial^2\bar{\theta}}{\partial r^2} + \frac{1}{r}\frac{\partial\bar{\theta}}{\partial r} = 0 \ . \tag{2}$$

The limiting reactant condition on the surface of the solid particles immediately specifys one boundary condition

$$\bar{\theta}(r = r_w) = 0 \ . \tag{3}$$

In the well-developed mass-transfer regions of the bed the fractional decrease of the reactant concentration and flux per period will be independent of position. This supplies the following boundary conditions

$$\bar{\theta}(r,1) = \bar{\theta}(r,0)e^{-\lambda} \tag{4}$$

$$\frac{\partial\bar{\theta}(r,1)}{\partial z} = \frac{\partial\bar{\theta}(r,0)}{\partial z}\ e^{-\lambda} \tag{5}$$

where λ is an eigenvalue of the solution to equations 2, 3, 4 and 5. The solution to this problem depends on the geometric parameters of the microscopic model r_A and A/r_A .

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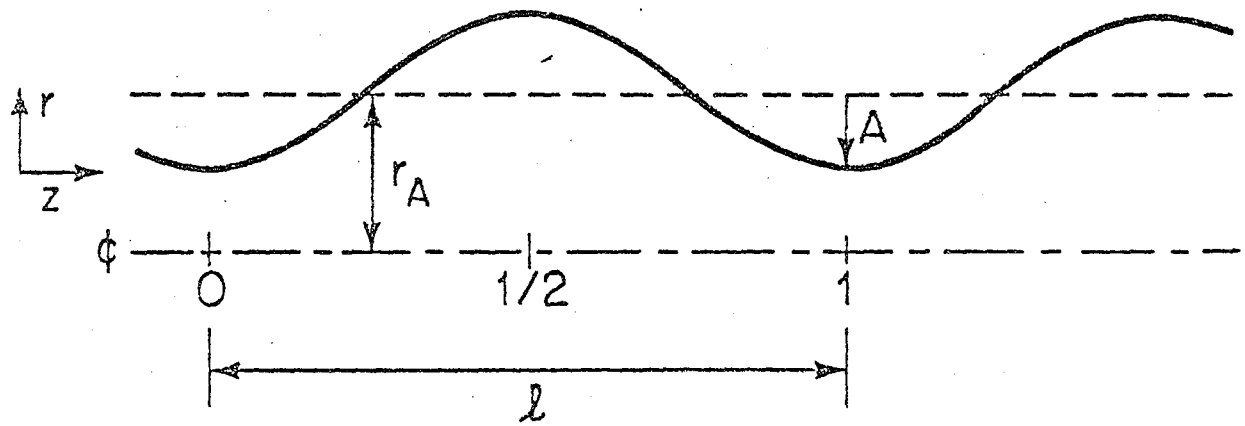

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Figure 1. The wall of a PCT generated by $r_w(z) = r_A - A \cos(2\pi z)$. All lengths are dimensionless with respect to the period length ℓ ,

For a deep bed, the eigenvalue λ can be related to the leading term of equation 1. The concentration variable at the exit of the reactor can be written as

$$\theta_L = \alpha_2 e^{-\lambda \frac{L}{\ell}} . \tag{6}$$

The PCT model yields the following geometrical relationship

$$\frac{L}{\ell} = \frac{r_A}{2} \frac{aL}{\varepsilon} \frac{2\varepsilon}{ar_{Ad}} . \tag{7}$$

Equations 6 and 7 can be substituted into the defining equation of the effective mass-transfer coefficient (eq. 1,1) to yield the analog of equation 1.

$$\frac{\varepsilon k_m}{a\mathcal{D}_o} = \frac{v}{a\mathcal{D}_o} \left[\frac{\lambda r_A}{2} \frac{2\varepsilon}{ar_{Ad}} - \frac{\varepsilon}{aL} \ln \frac{v}{\varepsilon a\mathcal{D}_o \alpha_2} \right]. \tag{8}$$

Thus the leading term α_1 of equation 1 can be calculated by finding the eigenvalue λ .

Method of Solution

An analytic solution for the eigenvalue problem determined by equations 2, 3, 4, and 5 could not be found. An approximate numerical scheme was used. The technique is similar to that utilized in earlier work (2). Laplace's equation and the boundary conditions are transformed into a new coordinate system (η,z) where $\eta = r/r_w(z)$. The wall boundary condition is then shifted to the coordinate curve $\eta = 1$.

A transformed concentration variable C was defined as

$$C = \bar{\theta} e^{\lambda z} \ . \tag{9}$$

This transformation was introduced in order to remove the eigenvalue from the boundary conditions and transfer it to the differential equation. Laplace's equation and its boundary conditions are then written as

$$C(\eta,0) = C(\eta,1) \tag{10}$$

$$\frac{\partial C(\eta,0)}{\partial z} = \frac{\partial C(\eta,1)}{\partial z} \tag{11}$$

$$C(1,z) = 0 \tag{12}$$

$$\frac{\partial^2 C}{\partial z^2} + \left[\frac{1}{r_w^2} + \eta^2\left(\frac{r_w'}{r_w}\right)^2\right]\frac{\partial^2 C}{\partial \eta^2} + \left[\frac{1}{\eta r_w^2} + \eta\left(2\left(\frac{r_w'}{r_w}\right)^2 - \frac{r_w''}{r_w} + 2\,\frac{r_w'}{r_w}\,\lambda\right)\right]\frac{\partial C}{\partial \eta} - \left[2\eta\,\frac{r_w'}{r_w}\right]\frac{\partial^2 C}{\partial \eta \partial z} - 2\lambda\,\frac{\partial C}{\partial z} + \lambda^2 C = 0 \ . \tag{13}$$

Two independent collocation procedures were used to solve equations 10 thru 13. These two techniques permitted a cross verification of the calculated results.

In the first method, an expansion for C was assumed in the form

$$C(\eta,z) = \sum_{k=1}^{NCP} A_k(z) J_o(\gamma_k \eta) \ . \tag{14}$$

Since the γ_k are the roots of the Bessel function J_o, this expansion identically satisfies the wall boundary condition. Equation 14 is

substituted into equation 13, and the residual is made equal to zero at NCP η collocation points. This generates a system of ordinary differential equations with the following boundary conditions

$$A_k(0) = A_k(1) \tag{15}$$

$$A_k'(0) = A_k'(1) \ . \tag{16}$$

Along with the normalization

$$A_1(0) = 1 \tag{17}$$

this specifies enough information to calculate the unknowns. Equation 13 was linearized and then solved by iteration on a z finite-difference grid using the method of Newman (3) slightly modified to exploit the storage space savings made possible by the periodic boundary conditions.

The second method uses a double series expansion to transform the original partial differential equation into a system of algebraic equations.

Since the A_k functions are periodic, they can be expanded in a Fourier series

$$A_k(z) = \sum_{m=1}^{NFC} (a_{km} \cos 2\pi(m - 1)z + b_{km} \sin 2\pi mz) \ . \tag{18}$$

The periodicity conditions are then identically satisfied. The unknown Fourier coefficients are determined by collocating the residual of a linearized equation 13 on a grid of NCP η points and 2NFC z

points. These collocation equations and the normalization condition specify a determinate system.

In both techniques the η collocation points were chosen to be evenly spaced in η^2 in the open interval (0,1) . The z points used in the double collocation method were chosen to be evenly spaced in the semi-open interval [0,1) . The collocation/finite difference method was computationaly advantageous for the larger values of the parameters reported here.

Results and Discussion

As seen from equation 8, the important quantity for calculating the Sherwood number is λr_A . Figure 2 presents the calculated values of λr_A in a sinusoidal PCT normalized by the value of λr_A (= 2.40482) for a straight wall cylinder.

Figure 3 presents results for the leading term of the Stanton number (Sh_B/Pe_B) in a mass-transfer controlled, deep-bed packed reactor modeled as an array of sinusoidal PCT. As the sinusoidal tube amplitude approaches zero for all values of r_A . The Stanton number approaches 1.202, the value for a straight wall tube.

Sørensen and Stewart (5) have calculated the asymptotic Stanton number for a bed of uniform sized spheres in simple cubic packing. In the terminology of this work, that number is found to be 1.233. As was found in the high Péclet number, asymptotic Sherwood number calculations and the friction factor calculations (2), a value of $r_A \sim 0.5$ and $A/r_A \sim 0.3$ to 0.4 for a sinusoidal PCT reproduce satisfactorily Sørensen and Stewart's results.

As has been emphasized, the above solution only generates the leading term of the deep-bed Stanton number. It is necessary to ask

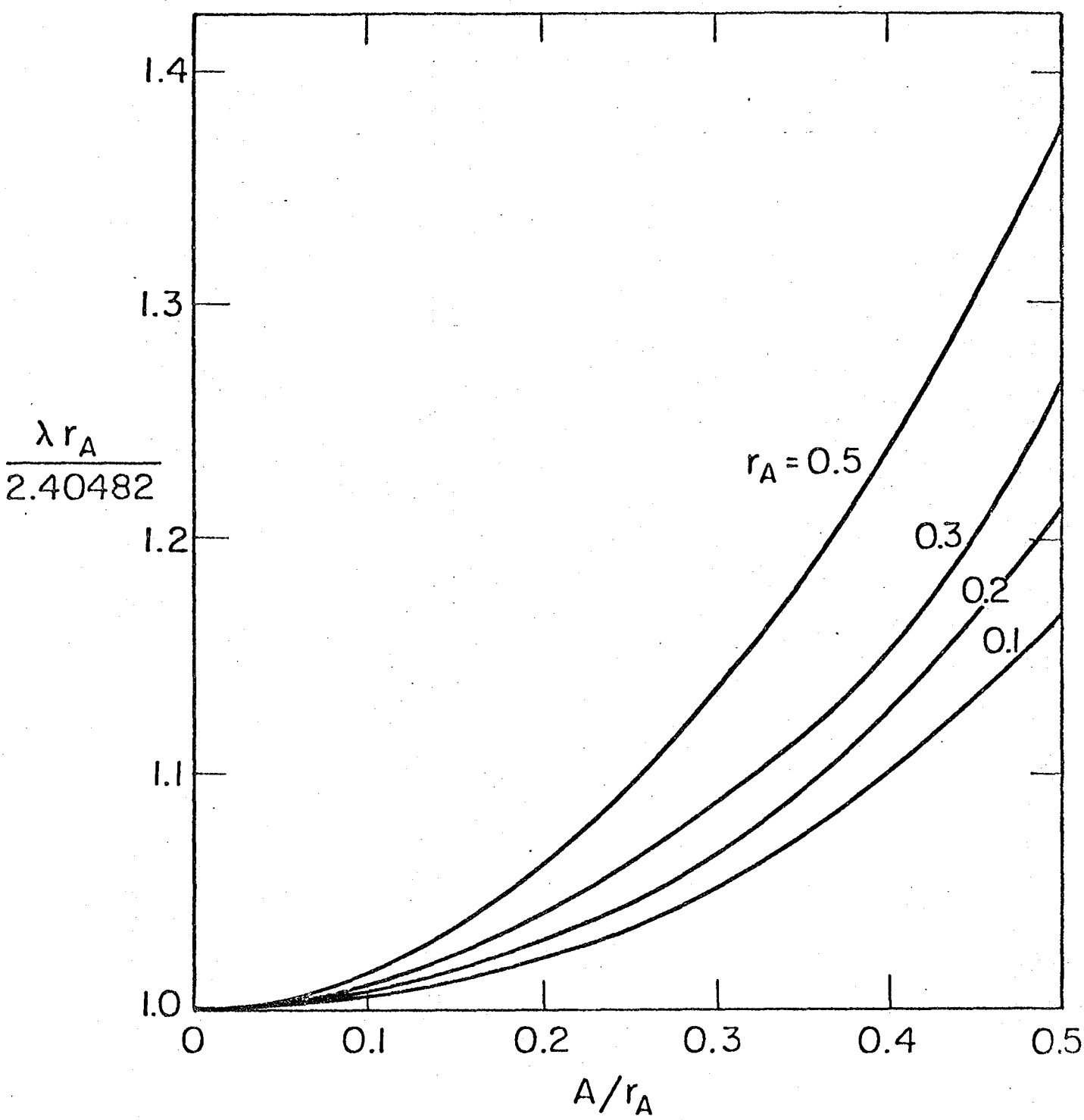

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Figure 2. The first eigenvalue of Laplace's equation in a sinusoidal PCT.

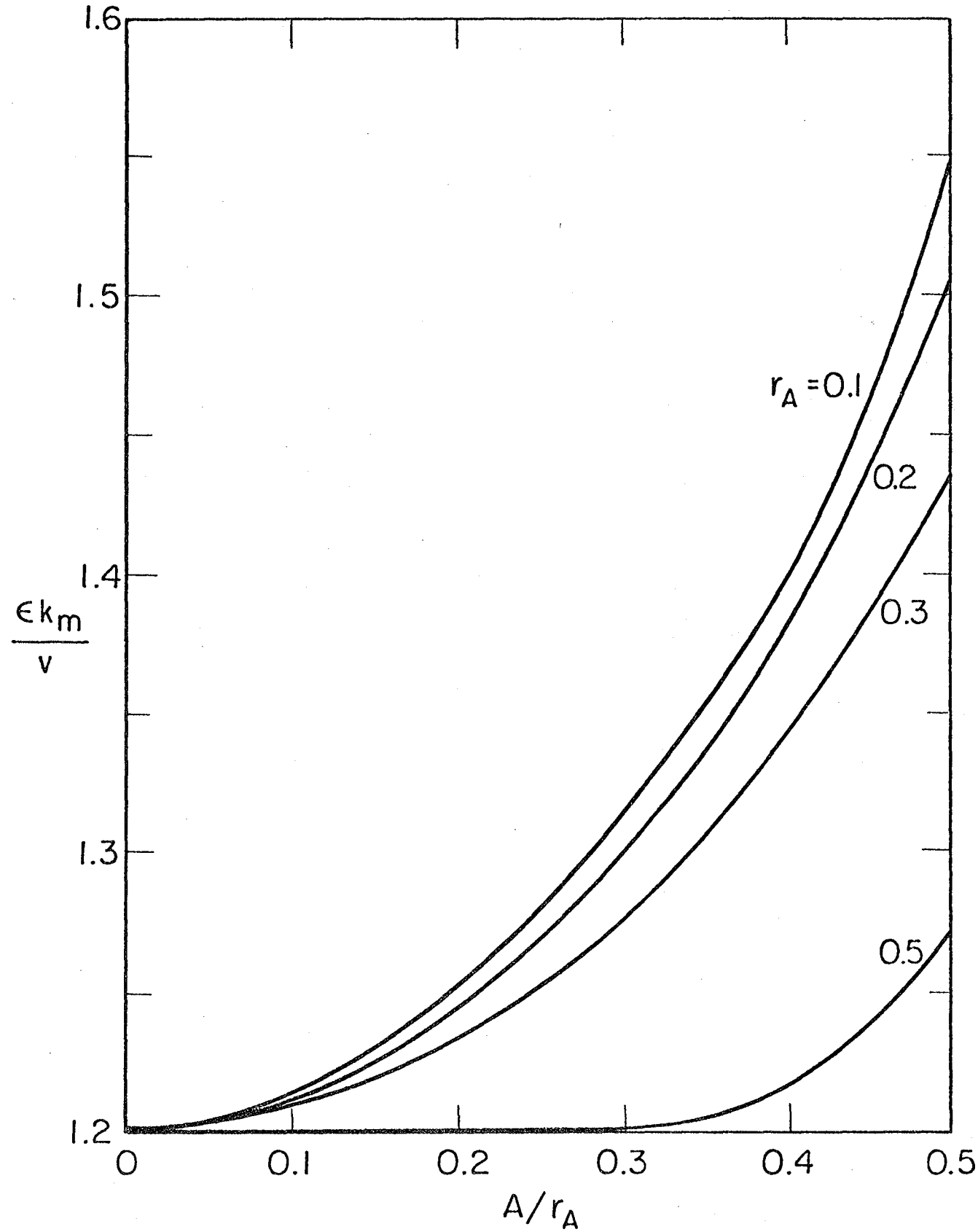

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Figure 3. Calculated values of the Stanton number for a mass-transfer controlled packed bed reactor in the low Péclet number region.

under what conditions can the second term of equation 1 be neglected. In order to calculate α_2 , the concentration variable in the entrance region of the bed must be calculated. This is an order of magnitude more difficult problem and is not attempted here. Sørensen and Stewart, however, have solved this problem for simple cubic packing of uniform spheres. We can use their results to estimate the effect of neglecting the second term in the expansion. Table 1 shows that for most bed depths with a Péclet number greater than 0.001, the error is acceptable. The error is seemingly further diminished in scale when a log-log plot of Sh_B vs Pe_B is examined.

The Stanton numbers presented above are for a non-diluted reactive bed. The reactive section of the bed must not contain an excess of inert particles. It should be emphasized that only under these conditions does Laplace's equation describe the concentration variable in the reactive section of the bed. For two beds with identical ε and aL values and with the same feed flowrate and concentration, one may argue, qualitatively, that the effective mass-transfer coefficient in the non-diluted bed must be greater than that in the diluted bed. Care must be taken in extrapolating low Péclet number mass-transfer coefficient experiments in diluted beds to non-diluted beds.

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Table 1

Sørensen and Stewart's results for the deep-bed, low Péclet number Stanton number of a simple cubic packed lattice of uniform size spheres

$\frac{\varepsilon k_m}{v}$

$\frac{v}{a\mathcal{D}_o}$ ↓ aL →	10	50	100	∞
1	1.165	1.219	1.226	1.233*
0.1	1.275	1.241	1.237	1.233*
0.01	1.384	1.263	1.248	1.233*
0.001	1.490	1.284	1.259	1.233*

*The low Péclet number, deep bed asymptote

$$\frac{\left(\frac{\varepsilon k_m}{v}\right) - \left(\frac{\varepsilon k_m}{v}\right)_{aL=\infty}}{\left(\frac{\varepsilon k_m}{v}\right)_{aL=\infty}} \times 100$$

$\frac{v}{a\mathcal{D}_o}$ ↓ aL →	10	50	100
1	-5.5	-1.1	-0.6
0.1	3.4	0.6	0.3
0.01	12.2	2.4	1.2
0.001	20.8	4.1	2.1

Notation

a	specific interfacial area, cm^{-1}
a_{km}, b_{km}	Fourier expansion coefficients
$A_k(z)$	unknown $k^{\underline{th}}$ expansion function, equation 14
A	dimensionless wall oscillation amplitude, A_d/ℓ
c	reactant concentration, m/cm^3
$\mathcal{C}$	transformation variable, equation 9
$\mathcal{D}_o$	free stream diffusion coefficient, cm^2/s
J_o	Bessel function of order zero
k_m	effective mass-transfer coefficient, cm/s
ℓ	length of PCT period, cm
L	length of reactive bed, cm
Pe_B	bed Péclet number $v/a\mathcal{D}_o$
r	dimensionless radial coordinate in a PCT, r_d/ℓ
r_A	dimensionless average PCT radius, r_{Ad}/ℓ
$r_w(z)$	dimensionless wall radius, r_{wd}/ℓ
Sh_B	bed Sherwood number, $\frac{\varepsilon k_m}{a\mathcal{D}_o}$
St_B	bed Stanton number Sh_B/Pe_B, $\frac{\varepsilon k_m}{v}$
v	superficial bed velocity, cm/s
z	dimensionless axial coordinate in a PCT, z_d/ℓ

Greek

α_1, α_2	constants of equation 1
γ_k	$k^{\underline{th}}$ root of Bessel function J_o
ε	bed porosity

$\bar{\theta}$ inner region expansion concentration variable $\frac{c\varepsilon}{c_F Pe_B}$

η $r/r_w(z)$

θ_L the outer limit of $\bar{\theta}_o$

λ eigenvalue of equations 10, 11, 12, 13

Subscripts

F feed condition at inlet of reactor

d dimensional quantity

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