Mass Transfer with Chemical Reaction from Single Gas Bubbles

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Numerical solutions of the equations that describe steady state, forced-convection mass transfer around single circulating or noncirculating gas bubbles have been obtained for both first- and second-order chemical reaction conditions. For the noncirculating bubbles, solutions have been obtained up to Reynolds numbers of 200 with Kawaguti velocity profiles used to describe the flow. In the case of circulating gas bubbles, Kawaguti profiles have been utilized up to Reynolds numbers of 80, while the potential flow velocity profiles have been used for higher Reynolds numbers. The numerical results for circulating gas bubbles have been compared with penetration theory for both first- and second-order chemical reactions. For the case of noncirculating gas bubbles the solutions for physical mass transfer have been compared with the Ranz and Marshall correlation as well as with the results of Griffith and the more recent work of Tsubouchi and Masuda.

The rates of mass transfer from single gas bubbles where the gas undergoes a chemical reaction in the continuous phase were studied. Transfer coefficients were calculated from numerical solutions of the equations that describe forced-convection mass transfer from both rigid and circulating gas bubbles. Both first- and second-order chemical reactions have been considered. Some experimental work has been carried out by Ward et al. (*1*) on liquid drops and by Griffith (*2*) on drops as well as gas bubbles, but in both cases only physical mass transfer was considered.

No solutions of the forced-convection mass transfer equation in spherical polar coordinates with simultaneous chemical reaction have previously been reported for Reynolds numbers greater than one. The numerical method employed for the first-order reaction case is an extension of a previous study by Johnson and Akehata (*3*) to the region of intermediate Reynolds numbers. For the second-order reaction situation the method employed by Brian and co-workers (*4, 5*) was followed. Their work was concerned with unsteady diffusion into a stagnant fluid with accompanying chemical reaction.

In order that the solution of the forced-convection mass transfer equation could be attempted it was essential to have relationships for the appropriate velocity profiles. In the study of mass transfer at very low Reynolds numbers by Johnson and Akehata (*3*), the Stokes (*6*) or Hadamard (*7*) velocity profiles were used. For the case of intermediate Reynolds numbers the velocity profiles obtained by Hamielec et al. (*9, 10*) were used. These profiles, which were obtained by solving the Navier-Stokes equation by using the Galerkin method, were found to be accurate up to the point of flow separation over the Reynolds number region described in this paper. This accuracy comparison was based on the solution of the Navier-Stokes equations by finite-difference techniques, extending the work of Jenson (*11*), and will be described in a separate paper.

THEORETICAL DEVELOPMENT

In deriving the equation that describes forced-convection mass transfer around a sphere the following assumptions were made: isothermal steady state conditions exist; the fluid is Newtonian and the flow is axisymmetric; the heat of reaction is negligible; density, viscosity, and diffusivities are constant; the bubbles are spherical and either noncirculating or fully circulating; the liquid phase is nonvolatile; chemical reaction is either first or second order; and mass transfer rates are small so that the radial velocity component is zero at the interface. Experimental work presently underway has indicated that a value for the radial velocity greater than 1% of the main stream velocity would be unusual for most gas liquid systems. Hamielec et al. (*20*) have shown that such values would be insufficient to affect the velocity profiles noticeably.

First-Order Chemical Reaction

Carrying out a mass balance on a spherical volume element as in reference 3 but neglecting molecular diffusion in the angular direction, we can write the resulting parabolic equation dimensionless form as

$$V_r \frac{\partial C_A}{\partial r} + \frac{V}{r} \frac{\partial C_A}{\partial \theta} = \frac{2}{N_{PeA}} \left[\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} - kC_A \right] \quad (1)$$

with boundary conditions

$$C_A = 1 \text{ at } r = 1$$

$$C_A = 0 \text{ at } r = \infty$$

$$\frac{\partial C_A}{\partial \theta} = 0 \text{ at } \theta = 0, \pi$$

If molecular diffusion in the angular direction had been included the resulting equation would have been elliptic in form. In both this work and the previous work of Akehata and Johnson (*3*), solutions of the elliptic equations could not be obtained for $N_{PeA} > 100$ because of numerical instabilities. It appeared that these instabilities could be suppressed only by using angular and radial step sizes that were too small to be practical.

Second-Order Reaction

Once again carrying out a mass balance on a spherical element and neglecting molecular diffusion in the angular direction as before, Equations (2) and (3) are obtained:

$$V_r \frac{\partial C_A}{\partial r} + \frac{V_\theta}{r}\frac{\partial C_A}{\partial \theta} = \frac{2}{N_{PeA}} \left[\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r} - k_A C_A C_B \right] \quad (2)$$

$$V_r \frac{\partial C_B}{\partial r} + \frac{V_\theta}{r}\frac{\partial C_B}{\partial \theta} = \frac{2}{N_{PeB}} \left[\frac{\partial^2 C_B}{\partial r^2} + \frac{2}{r}\frac{\partial C_B}{\partial r} - k_B C_A C_B \right] \quad (3)$$

With boundary conditions

$$C_A = 1, \frac{\partial C_B}{\partial r} = 0 \text{ at } r = 1$$

$$C_A = 0, C_B = 1 \text{ at } r = \infty$$

$$\frac{\partial C_A}{\partial \theta} = \frac{\partial C_B}{\partial \theta} = 0 \text{ at } \theta = 0, \pi$$

The velocity components as given by Hamielec et al. (*10*) are

$$V_\theta = \left(1 - \frac{A_1}{r^3} - \frac{2A_2}{r^4} - \frac{3A_3}{r^5} - \frac{4A_4}{r^6}\right) \sin\theta + \left(-\frac{B_1}{r^3} - \frac{2B_2}{r^4} - \frac{3B_3}{r^5} - \frac{4B_4}{r^6}\right) \sin\theta \cos\theta \quad (4)$$

$$V_r = -\left(1 + \frac{2A_1}{r^3} + \frac{2A_2}{r^4} + \frac{2A_3}{r^5} + \frac{2A_4}{r^6}\right) \cos\theta - \left(\frac{B_1}{r^3} + \frac{B_2}{r^4} + \frac{B_3}{r^5} + \frac{B_4}{r^6}\right) (2\cos^2\theta - \sin^2\theta) \quad (5)$$

where

$$A_2 = \left(\frac{-125 - 120X}{60 + 29X}\right) + \left(\frac{-140 - 75X}{60 + 29X}\right) A_1 \quad (6)$$

$$A_3 = \left(\frac{135 + 153X}{60 + 29X}\right) + \left(\frac{108 + 63X}{60 + 29X}\right) A_1 \quad (7)$$

$$A_4 = \left(\frac{-40 - 47.5X}{60 + 29X}\right) + \left(\frac{-28 - 17X}{60 + 29X}\right) A_1 \quad (8)$$

$$B_2 = \left(\frac{-140 - 69X}{60 + 27X}\right) B_1 \quad (9)$$

$$B_3 = \left(\frac{108 + 57X}{60 + 27X}\right) B_1 \quad (10)$$

$$B_4 = \left(\frac{-28 - 15X}{60 + 27X}\right) B_1 \quad (11)$$

X is the ratio of the viscosity of the dispersed phase to that of the continuous phase. Values of A_1 and B_1 are tabulated at several Reynolds numbers by Hamielec et al. (*10*).

The desired numerical solutions are obtained in the form $C_A = f_1(r,\theta)$, $C_B = f_2(r,\theta)$, and the local Sherwood numbers can be calculated from

$$N_{Sh} = -2 \left[\frac{\partial C_A}{\partial r}\right]_{r=1} \quad (12)$$

NUMERICAL TECHNIQUES

First-Order Reaction

The Crank-Nicholson implicit method (*13*) was employed in the solution of Equation (1). In this method the partial derivatives in the radial direction are replaced by the average of the derivatives at the points i, j, and $i, j + 1$. The mesh system, utilizing a variable step size in the radial direction as in reference *3*, is shown in Figure 1.

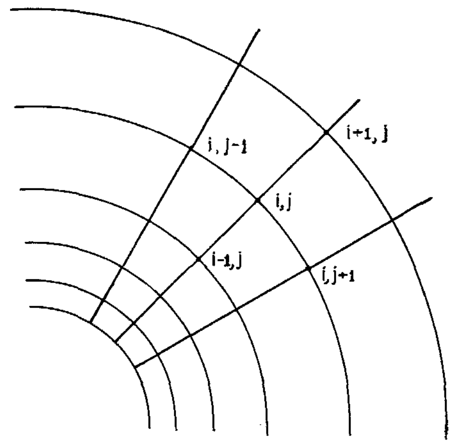

Fig. 1. Finite-difference mesh system.

The finite-difference equation obtained, corresponding to Equation (1), is the Equation (14) used by Johnson and Akehata (*3*) and is similar to Equation (13) here. Initially, results were obtained by using a relaxation factor and an iterative procedure but later solutions were obtained more rapidly by inverting a tridiagonal matrix at each angular increment.

Second-Order Reaction

Writing Equations (2) and (3) according to the Crank-Nicholson approximation, we can write the finite-difference equation (replacing C_A by A and C_B by B) as

$$A^*_{i+1,j}[l_1 - l_2 - l_3] + A^*_{i-1,j}[-l_1 - hl_2 - l_3] + A_{i+1,j+1}[l_1 - l_2 - l_3] + A_{i-1,j+1}[-l_1 - hl_2 + l_3] + A_{i,j+1}\left[l_4 + l_5 + \frac{k_A B_{i,j+1/2}}{N_{PeA}}\right] + A^*_{i,j}\left[-l_4 + l_5 + \frac{k_A B_{i,j+1/2}}{N_{PeA}}\right] = 0 \quad (13)$$

$$B^*_{i+1,j}[l_1 - l_2 - l_3] + B^*_{i-1,j}[-l_1 - hl_2 + l_3] + B_{i+1,j+1}[l_1 - l_2 - l_3] + B_{i-1,j+1}[-l_1 - hl_2 + l_3] + B_{i,j+1}[l_4 + l_5 + k_B A_{i,j+1/2}/N_{PeB}] + B^*_{ij}[-l_4 + l_5 + k_B A_{i,j+1/2}/N_{PeB}] = 0 \quad (14)$$

where

$$\begin{aligned} l_1 &= V_r/(2h^{i-1}\Delta r\,(1 + 1/h)) \\ l_2 &= 2/h(h^{i-1}\Delta r)^2\,(1 + 1/h)\,N_{PeA} \\ l_3 &= 2/(h^{i-1}\Delta r)\,(1 + 1/h) r_i N_{PeA} \\ l_4 &= V_\theta/r_i\,\Delta\theta \\ l_5 &= 2(1+h)/(h^{i-1}\Delta r)^2(1 + 1/h)\,N_{PeA} \\ l_6 &= k/N_{PeA} \end{aligned} \quad (15)$$

and the starred quantities are known values.

The method employed in solving these equations is due to Douglas (*14*) and the procedure and its advantages have been outlined by Brian et al. (*4*). The one variation in this work was the use of the DuFort-Frankel (*15*) form in the explicit step rather than the usual forward difference approximation, since the latter proved to be unstable in this instance. Thus Equation (3) is written as

$$B_{i+1,j}[l_1/2 - 2l_2 - 2l_3] + B_{ij}[l_4/2 - l_5/2 + 2k_B A_{ij} N_{PeB}] + B_{i-1,j}[-l_1/2 - 2hl_2 + 2l_3] + B_{i,j-1}[-l_4/2 - l_5/2] + B_{i,j+1/2}[l_4 - l_5] = 0 \quad (16)$$

Using Equation (16) we solve the $B_{i,j+1/2}$ values directly and substitute them into Equation (14). The $A_{i,j+1}$ values can then be readily obtained by inverting the resulting tridiagonal matrix, and then the $A_{i,j+1/2}$ values are obtained from

$$A_{i,j+1/2} = \frac{A_{i,j+1} + A_{ij}}{2} \tag{17}$$

By inserting these values into Equation (15), the $B_{i,j+1}$ are obtained by matrix inversion.

Over the next angular increment the procedure was reversed with the $A_{i,j+1/2}$ first obtained from the DuFort-Frankel explicit form of Equation (2). By inserting these values into Equation (15), the $B_{i,j+1}$ values are obtained, followed by the calculation of the $B_{i,j+1/2}$ from

$$B_{i,j+1/2} = \frac{B_{i,j+1} + B_{ij}}{2} \tag{18}$$

Finally, substituting these values into Equation (14), we obtain the $A_{i,j+1}$ by matrix inversion.

RESULTS AND DISCUSSION

Angular increments of 3 deg. were used in the finite-difference mesh system and the magnitude of the first step in the radial direction was 5×10^{-5} dimensionless radii. The location of the outer limit of the mesh system was usually 0.44 dimensionless radii from the sphere surface. Placing the outer boundary at a greater distance from the sphere surface did not affect the calculated Sherwood numbers. Extensive checks on the accuracy of the numerical solutions were carried out. If, for example, the normally used mesh size noted above was halved, thus doubling the number of mesh points, the numerical results remained unchanged within 1%. As a result of many similar checks it is felt that convergence of the numerical solutions has been obtained.

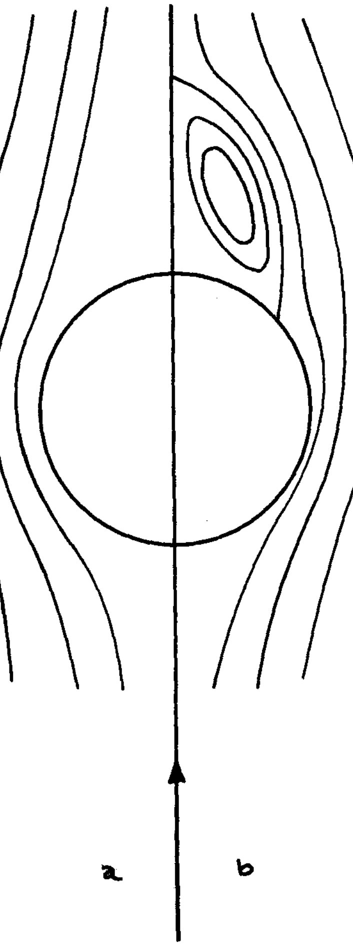

Fig. 2a. Streamlines around a circulating gas bubble at intermediate Reynolds numbers. Fig. 2b. Streamlines around a noncirculating gas bubble at intermediate Reynolds numbers.

To satisfy the boundary condition $\partial C/\partial \theta = 0$ at $\theta = 0$, it was necessary to use an iteration technique in starting the Crank-Nicholson procedure. Estimates of the concentrations were inserted along the first two radial vectors and the marching solution allowed to proceed through the first step in the θ direction. The values obtained were used as better estimates of the values at $\theta = 0$. This procedure was repeated until the condition $\partial C/\partial \theta = 0$ had been satisfied to a specified tolerance.

As has been previously pointed out, by neglecting molecular diffusion in the angular direction, we can obtain parabolic equations which can be solved by existing numerical techniques. The parabolic equation however does not everywhere describe the physical situation accurately. In the case of flow around circulating gas bubbles (Figure 2*a*) Equations (1), (2), and (3) hold everywhere except very near the poles. This drawback is not serious and accurate local Sherwood numbers can be obtained over the whole sphere surface with little difficulty. However for the case of flow around noncirculating gas bubbles (for example, where the interface is motionless due to the accumulation of surfactant) or rigid spheres as shown in Figure 2*b*, the neglected angular diffusion terms become extremely important at the point of flow separation. It has therefore been possible to obtain local mass transfer rates only up to the separation point for the rigid sphere case and it has been necessary to make an assumption regarding local mass transfer rates in the vortex region. In this work it has been assumed that there is no mass transfer beyond the separation point and average Sherwood numbers for the entire sphere surface were obtained by using zero for the local Sherwood numbers in the vortex region. There was one exception to this which arose in the case of very fast first-order chemical reaction. Under these conditions the mass transfer rates became independent of the hydrodynamics and numerical solutions were obtained beyond the separation point. These solutions, as expected, corresponded to the solution of the equation describing diffusion from a sphere into a stagnant fluid with first-order chemical reaction.

Circulating Gas Bubbles

It was found that the numerical results for physical mass transfer at Reynolds numbers > 200 agreed with the solution of the Boussinesq (*17*) equation as expected. The complete results for both first- and second-order reaction are presented in terms of the enhancement factor vs. $\sqrt{M}$ in Figure 3. This allows for direct comparisons with the penetration theory results, including the numerical results obtained by Brian (*4*). It is seen that in all cases the solutions obtained in this work agree with penetration theory. The situations covered were for the first-order case, Reynolds numbers from 20 to 500, $N_{Sc_A} = 500$, and dimensionless reaction rates from 0 to 10^6. For the second-order reaction situation the cases studied were as follows:

1. $N_{Re} = 20$ to 80, $N_{Sc_A} = 500$, $N_{Sc_B} = 800$
   $k_A = 10^6, k_B = 10^5; k_A = 10^4, k_B = 10^3; k_A = 10^2, k_B = 10$
2. $N_{Re} = 20$ to 500, $k_A = k_B = 10^6$
   $N_{Sc_A} = N_{Sc_B} = 100, 500, 1000$

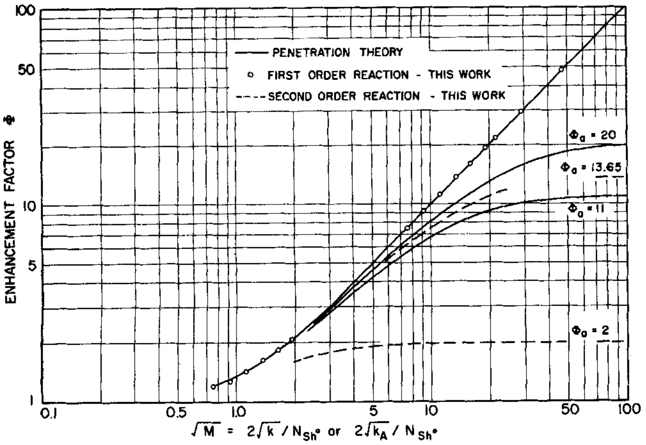

Fig. 3. Comparison of results for circulating gas bubbles with penetration theory.

The limiting enhancement factor for infinitely fast reaction ϕ can be calculated from (*4*)

$$\phi_a = 1 + \frac{\overset{o}{C_B}}{C^s_A}\sqrt{\frac{D_B}{D_A}} = 1 + \frac{k_A}{k_B}\sqrt{\frac{N_{ScB}}{N_{Sc_A}}} \quad (19)$$

For case 1 ϕ_a is equal to 13.65, whereas for case 2 ϕ_a is equal to 2.0. In both cases the calculated ϕ values are seen to approach these limiting values as expected.

It can be tentatively concluded that mass transfer with or without chemical reaction from circulating gas bubbles can be described very well by penetration theory. This then makes it possible to deal with the simpler penetration theory equations rather than the more complex ones [Equations (1), (2), and (3)] dealt with in this work.

Noncirculating Gas Bubbles

When the local mass transfer rates for physical mass transfer calculated from this work were compared with the values obtained analytically by Baird and Hamielec via the thin concentration boundary-layer assumption, excellent agreement was obtained. An example is shown in Figure 4. The average Sherwood numbers obtained for physical mass transfer are compared in Figure 5 with the well-known correlations of Ranz and Marshall (*16*), Tsubouchi and Masuda (*19*), as well as with an average of all the data obtained by Griffith (*2*). If when calculating the average Sherwood number from the numerical results it is assumed that there is no mass transfer beyond the separation point, very good agreement is obtained with the experimental results of these workers. The results for first- and second-order chemical reaction are presented in terms of enhancement factors in Figure 6. It can be seen that as the Reynolds number increases, the second-order values approach those of first-order reaction. This is expected, since as the Reynolds number increases the reactant present in the bulk of the fluid is brought into the reaction zone by forced convection more rapidly and pseudo first-order behavior is approached. No experimental results are available for mass transfer with chemical reaction from noncirculating spheres and therefore the applicability of these results to this situation cannot be confirmed at this time. An experimental study investigating mass transfer with second-order reaction from noncirculating gas bubbles will be reported in a later paper.

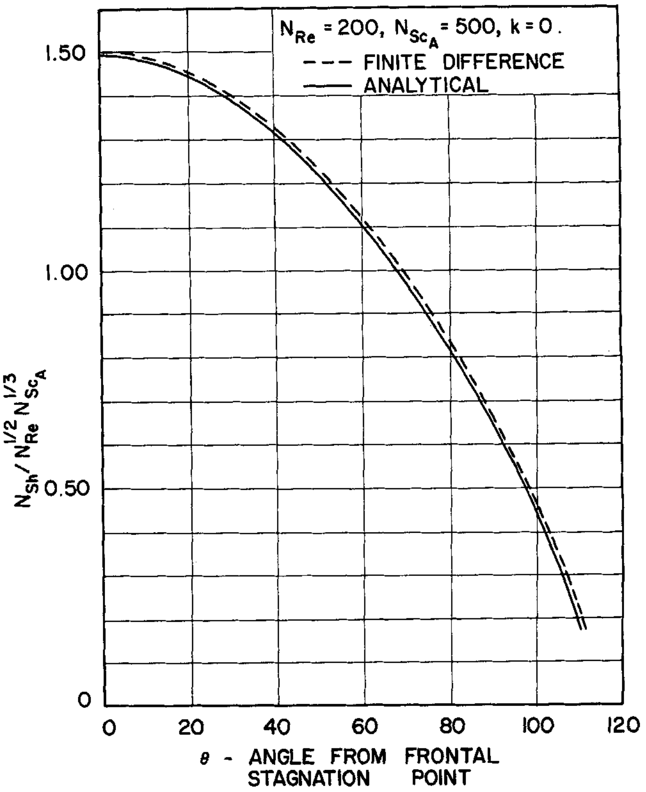

Fig. 4. Comparison of local Sherwood number values obtained numerically with those obtained by Baird and Hamielec; rigid spheres.

It should be noted that numerical instabilities were encountered when the dimensionless reaction rate k_A was greater than 10^4. This difficulty occurs at a certain point in the calculations where it is necessary to subtract two large numbers of the same order of magnitude, resulting in a small inaccurate residual. It was found that if the DuFort-Frankel approximation for the derivative $\partial^2 C/\partial r^2$ was used in the implicit step (it was always necessary to use this form in the explicit step) the source of the instability could be removed. No problems of this nature

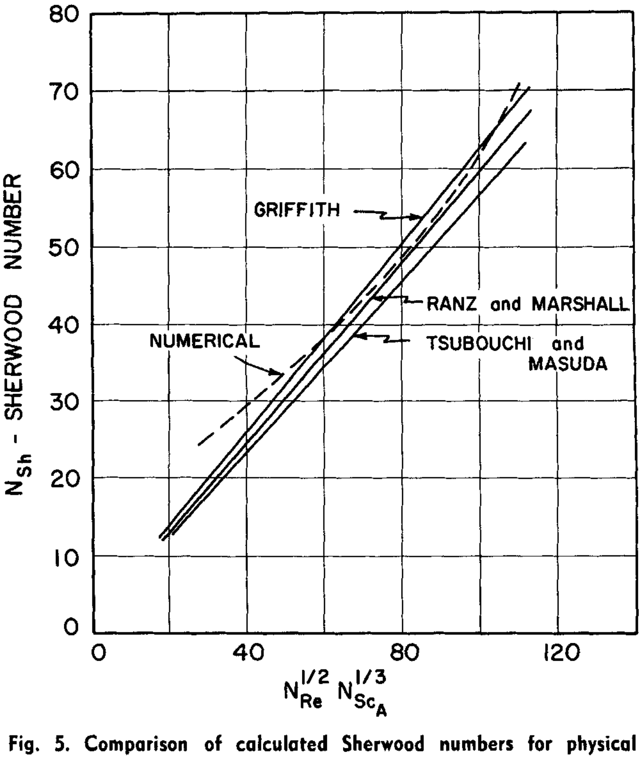

Fig. 5. Comparison of calculated Sherwood numbers for physical mass transfer with experimental correlations; rigid spheres.

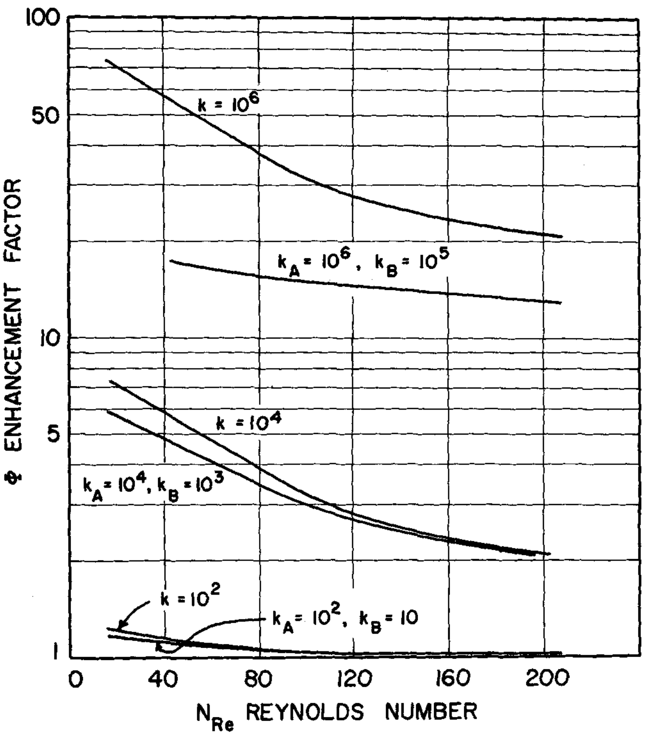

Fig. 6. Enhancement factors for mass transfer with first- and second-order chemical reaction from rigid spheres.

were encountered when dealing with the circulating gas bubble case.

CONCLUSIONS

Solutions of the equations that describe forced-convection mass transfer from single spheres have been obtained for both first- and second-order chemical reaction situations. The results for circulating gas bubbles are in excellent agreement with penetration theory. Predicted physical mass transfer rates for spheres compare favorably with the experimental results of other workers. Additional experimental data are required to corroborate the numerically predicted mass transfer rates from rigid spheres with first- or second-order reaction.

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NOTATION

A_i, B_i = coefficients in Equations (4) to (11)
A_{ij}, B_{ij} = concentrations of reactants in finite-difference equations (14), (15), and (16), dimensionless
C_A = concentration of material transferred from the sphere into the liquid, dimensionless
C_B = concentration of reactant originally present in liquid phase, dimensionless
C^s_A = saturation concentration of material A in liquid phase, moles/liter
C^o_B = concentration of material B in bulk of fluid, moles/liter
D_A, D_B = binary diffusion coefficients of A and B in nonreacting solvent, sq.cm./sec.
h = constant greater than unity
k = R^2k_1/D_A, dimensionless reaction rate constant for first-order reaction
k_1 = reaction rate constant for first-order reaction, sec.$^{-1}$
k_2 = reaction rate constant for second-order reaction, liters/(mole)(sec.)
k_A = $R^2k_2C^o_B/D_A$, dimensionless reaction rate constant for second-order reaction
k_B = $R^2k_2C^s_A/D_B$, dimensionless reaction rate constant for second-order reaction
k_L = liquid phase mass transfer coefficient, cm./sec.
l_i = coefficients in Equations (13), (14), (15), and (16).
$\sqrt{M}$ = $2\sqrt{k}/N_{Sh^o}$ for first-order reaction; or $2\sqrt{k_A}/N_{Sh^o}$ for second-order reaction
N_{Re} = $2RU\rho/\mu$, Reynolds number
N_{ScA} = $\mu/\rho D_A$, Schmidt number for material A
N_{ScB} = $\mu/\rho D_B$, Schmidt number for material B
N_{Sh^o} = $2Rk^o_L/D_A$, Sherwood number for mass transfer without chemical reaction
N_{Sh} = $2Rk_L/D_A$, Sherwood number for mass transfer with chemical reaction
r = distance from center of sphere, dimensionless
R = radius of sphere, cm.
U = main stream velocity, cm./sec.
V_r = radial velocity component, dimensionless
V_θ = tangential velocity component, dimensionless
X = viscosity ratio, dispersed phase/continuous phase

Greek Letters

μ = viscosity of continuous phase, poise
ρ = density of continuous phase, g./cc.
θ = polar angle, rad.
ϕ = N_{Sh}/N_{Sh^o}, enhancement factor
ϕ_a = limiting enhancement factor for infinitely fast second-order reaction

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