Mass Transfer with Homogeneous Chemical Reaction in Turbulent Pipe Flow

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Mass transfer with chemical reactions in fully developed turbulent pipe flows has been studied theoretically. The pipe walls are assumed to remain at a constant prescribed concentration. The effect of arbitrary reaction orders and of Reynolds and Schmidt numbers upon the transfer coefficients was investigated. Radial and longitudinal concentration profiles were obtained to show the effect of reaction orders and dimensionless rate constants. Effects of concentration levels on these phenomena were also studied and proven significant. The ratio of the transfer coefficients with chemical reactions to those without chemical reactions increases as a function of the downstream aspect ratio.

In many chemical engineering operations the process of mass transfer consists of the diffusion of a solute through a nondiffusing gas stream. Although many industrial operations, such as chemical absorption and desorption processes, involve simultaneous mass transfer and a chemical reaction, most of the work dealt with pure mass transfer. In operations it is also necessary to know the gas phase transfer coefficients for short contacting sections, as this is normally the most efficient method of obtaining the desired transfer.

Most of the work in mass transfer with chemical reaction has been in predicting changes of the transfer coefficient using the following theories:

1. The film theory first proposed by Hatta (*5*). This theory was extended to turbulent systems by Sherwood and Ryan (*9*), Meyerink and Friedlander (*7*), and Marangonis et al. (*6*), by using the analogy theory in conjunction with the film theory. Veith, Porter, and Sherwood (*14*) extended the work by analyzing first order systems in turbulent flows. Szekely (*11*) incorporated the bulk flow effect in a simple laminar flow system.
2. The penetration-surface renewal models proposed by Danckwerts (*2*).
3. A theory was proposed by Toor and Chiang (*13*) and later extended by Toor (*12*) to incorporate a number of systems in dilute turbulent and nonturbulent regimes.
4. The laminar boundary-layer theory, first used by Friedlander and Litt (*4*) for flat plates and later extended by Acrivos (*1*) for wedge flows.

Another interesting problem is the role of the concentration levels in the rate of transfer and reaction of the solute. Wasan and Wilke (*16*) conducted a detailed study which showed the substantial effect of concentration levels on mass transfer in turbulent systems.

It is the purpose of this analysis to obtain theoretical solutions of the diffusion-convection equations for the case of convective mass transfer accompanied by a homogeneous chemical reaction, from a cylindrical tube into a fully developed turbulent flow, in the presence of a finite crossflow velocity due to bulk diffusion effects. Thus, the role of arbitrary reaction orders, rate constants, and the concentration level of nondiffusion species on the mass transfer rates can be established.

THEORETICAL ANALYSIS

Equation of Convective Diffusion

Consider the case of transfer of a potentially reactive fluid *A* from a tube wall across a mass transfer section of finite length into which varying amounts of another potentially reactive fluid *B* enters with a fully developed, turbulent, velocity distribution. An arbitrary-order homogeneous reaction starts the instant fluids *A* and *B* come into contact with each other. Component *A* is maintained at a constant concentration at the wall over the entire section. Mass transfer occurs by diffusion and also by bulk transport of material by a velocity in the radial direction. Assume that the azimuthal components can be neglected. Axial diffusion is assumed to be negligible at all aspect ratios. Schneider's theoretical analysis (*8*) and the recent computational analysis performed by Wasan et al. (*18*) support this assumption.

On the basis of these assumptions, consideration of a differential volume of fluid results in the following convective-diffusion equation:

$$U\rho_t \frac{\partial W_A}{\partial x} + V\rho_t \frac{\partial W_A}{\partial r} = \frac{\rho_t}{r} \frac{\partial}{\partial r}\left[(D+E) r \frac{\partial W_A}{\partial r} \right] + R_A \tag{1}$$

Diffusion of Solute

In the present case of the diffusion of a solute the transfer mechanism can be approximated as that of diffusion; the solute reacts through fluid *B*, which exhibits no net transfer in the direction of solute transfer, i.e., assume the flux of *B* is zero. Strictly speaking, the net flux of the

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inert component B is zero only at the axis and the tube wall. However, it has been noticed in most transport processes at ordinary mass transport rates that the transfer mechanism approximated by $N_B = 0$ at every radial position is readily applicable.

Wasan and Wilke (*16*) made a detailed analysis of this assumption and found it to hold true. For mass transfer in a system with $N_{Sc} = 1.0$, $N_{Re} = 10{,}000$ and $X_f = 0.69$, the maximum value of $N_B/N_B + N_A$ did not exceed 4.7×10^{-4}.

$$N_B = -\,(D+E)\rho_t \frac{\partial W_B}{\partial r} + W_B\,(\rho_A V_A + \rho_B V_B) = 0 \tag{2}$$

Because the velocity in the radial direction can be written as

$$V = \frac{\rho_A V_A + \rho_B V_B}{\rho_t} \tag{3}$$

Equation (2) can be rearranged to give

$$V = -\frac{(D+E)}{(1-W_A)}\,\frac{\partial W_A}{\partial r} \tag{4}$$

Note that the radial velocity is zero at the tube axis because the concentration gradient is zero, and that the radial velocity is maximum at the pipe wall. This has been analyzed in detail by Wasan and Wilke (*16*). The momentum profiles, however, are assumed to be unaffected by the occurrence of this radial diffusion velocity. Observations of the fully developed turbulent velocity fields in the presence of moderate mass transfer rates revealed no significant effect of mass transfer on the velocity distribution (*17*).

For an arbitrary-order homogeneous reaction the rate of depletion of a species can be written

$$R_A = -\,k_n \rho_t^{\,n} W_A^{\,n} \tag{5}$$

Substituting Equations (4) and (5) into (1) and using the S-transformation [Solbrig and Gidaspow (*10*)] which expands the wall region and contracts the turbulent core region,

$$S = \frac{S^+}{S_0^+} = \int_0^{y^*} \frac{dy^*}{\dfrac{\rho_t}{\mu}(D+E)} \Bigg/ \int_0^{1} \frac{dy^*}{\dfrac{\rho_t}{\mu}(D+E)}$$

We obtain

$$\frac{\partial W_A}{\partial x^*} = \frac{2}{U^* N_{Re}\left(\dfrac{1}{N_{Sc}} + \dfrac{\epsilon}{\nu}\right) S_0^{+2}}\,\frac{\partial^2 W_A}{\partial S^2} - \frac{2}{U^* N_{Re}(1-y^*)S_0^+}\,\frac{\partial W_A}{\partial S} + \frac{2}{U^* N_{Re}(1-W_A)\left(\dfrac{1}{N_{Sc}} + \dfrac{\epsilon}{\nu}\right) S_0^{+2}}\left(\frac{\partial W_A}{\partial S}\right)^2 - \frac{K}{U^*}\,W_A^{\,n} \tag{6}$$

where

$$K = \frac{k_n \rho_t^{\,n-1} R}{U_{av}}$$

is a dimensionless rate constant, and

$$X^* = \frac{x}{R}$$

To better understand the mass transfer aspect of the problem, it is convenient to express the concentration in the dimensionless form

$$W^+ = \frac{W_A - W_{A0}}{W_{AW} - W_{A0}}$$

Equation (6) can be rewritten

$$\frac{\partial W^+}{\partial x^*} = \frac{2}{U^* N_{Re}\left(\dfrac{1}{N_{Sc}} + \dfrac{\epsilon}{\nu}\right) S_0^{+2}}\,\frac{\partial^2 W^+}{\partial S^2} - \frac{2}{U^* N_{Re}(1-y^*)S_0^+}\,\frac{\partial W^+}{\partial S} + \frac{2}{U^* N_{Re}\left(\dfrac{1-W_{A0}}{W_{AW}-W_{A0}} - W^+\right)\left(\dfrac{1}{N_{Sc}} + \dfrac{\epsilon}{\nu}\right) S_0^{+2}}\left(\frac{\partial W^+}{\partial S}\right)^2 - \frac{K(W^+(W_{AW}-W_{A0}) + W_{A0})^n}{U^*(W_{AW}-W_{A0})} \tag{7}$$

Boundary Conditions

The boundary conditions of the system to be studied can be expressed in dimensionless form:

1. The concentration at the inlet is constant, or $W^+(S, 0) = W_0^+$.
2. There is no concentration gradient at the axis of the tube and the profile is symmetric, or $\partial W^+/\partial S\ (1, x^*) = 0$.
3. The concentration at the wall is constant for all downstream distances, or $W^+(0, x^*) = 1.0$.

The velocity and eddy viscosity distributions to be used in the analysis have been detailed by Wasan, Tien, and Wilke (*15*).

Numerical Analysis

A finite difference, marching integration technique was used by applying the explicit scheme suggested by Dufort and Frankel (3). Using this model results in a finite difference equation corresponding to Equation (7):

$$\begin{aligned} W(I+1,J) &= W(I-1,J) + AA(J)\,[W(I,J+1) + W(I,J-1) - 2W(I-1,J)] \\ &\quad - B(J)\,[W(I,J+1) - W(I,J-1)] \\ &\quad + \frac{AA(J)}{4(D - W(I,J))}\,[W(I,J+1) - W(I,J-1)]^2 \\ &\quad - \frac{2K\Delta x^*}{U^*(W_w - W_0)(1-A(J))}\,[W(I,J) \cdot (W_w - W_0) + W_0]^n \end{aligned} \tag{8}$$

where

$$D = \frac{1 - W_{A0}}{W_{Aw} - W_{A0}}, \qquad AA(J) = \frac{A(J)}{1 - A(J)}$$

$$A(J) = \frac{4\,\Delta x^*}{N_{Re}\,U^*\left(\dfrac{1}{N_{Sc}} + \dfrac{\epsilon}{\nu}\right) S_0^{+2}\,\Delta S^2}$$

and

$$B(J) = \frac{2\,\Delta x^*}{N_{Re}\,U^*\,(1-y^*)(1-A(J))\,S_0^+\,\Delta S}$$

At the center line of the tube, y^* goes to unity and the denominator term $(1 - y^*)$ goes to zero, as does the first derivative of the mass fraction in the numerator.

Using L'Hopital's rule, and because of negligible stability problems, Equation (8) can be re-expressed in a simple explicit formulation

$$\begin{aligned} W(I+1, JEND) &= W(I, JEND) \\ &+ 2A(J)\,[W(I, JEND-1) - W(I, JEND)] \\ &- \frac{2K\Delta x^*}{U^*\,(W_w - W_0)\,(1 - A(J))} \\ &[W(I, JEND)\cdot(W_w - W_0) + W_0]^n \qquad (9) \end{aligned}$$

Where $J = JEND$ for center-line grid position.

Equations (8) and (9), with the boundary conditions listed earlier, can be solved once $A(J)$ and $B(J)$ are obtained.

The local Stanton number is defined as

$$N_{St} = \frac{k_g}{U_{av}}$$

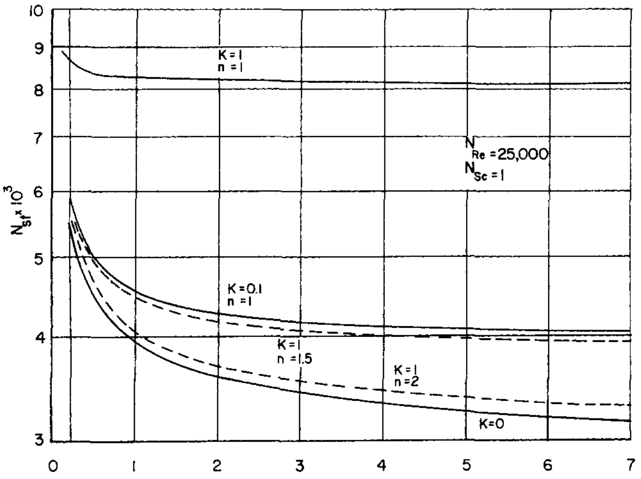

Fig. 1. Effect of various reaction orders and dimensionless rate constants on Stanton numbers for downstream aspect ratios.

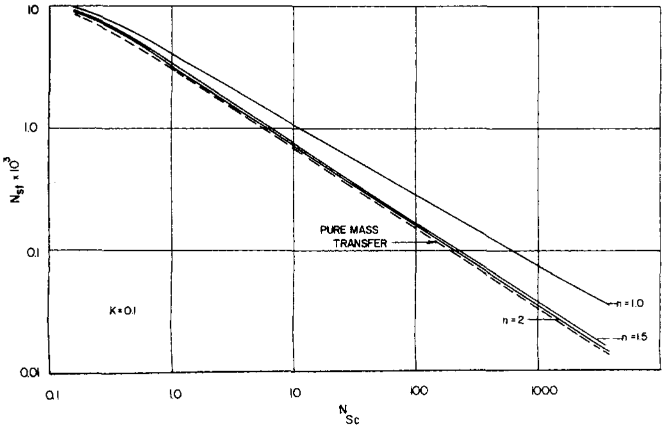

Fig. 2. Effect of reaction orders on Stanton numbers for varying Schmidt numbers.

where, by assuming constant density, the mass transfer coefficient is

$$N_A = \frac{-D\rho_t\left(\frac{\partial W_A}{\partial r}\right)_{r=R}}{(1 - W_A)_{r=R}} = k_g\rho_t(W_{AW} - W_{A_{av}})$$

Substituting the above equations, the final expression for Stanton numbers is obtained

$$N_{St} = \frac{2\left(\frac{\partial W_A}{\partial y^*}\right)_{y^*=0}}{N_{Sc}N_{Re}(1 - W_{AW})(W_{AW} - W_{A_{av}})} \qquad (10)$$

RESULTS AND DISCUSSION

Concentration profiles and local Stanton numbers were computed over a range of reaction orders, dimensionless rate constants, and Reynolds and Schmidt numbers. In the test system the difference between incoming and wall concentrations was set at 10 mm. (unless otherwise specified) with the inlet condition at 1 atm.

Figure 1 shows the change in Stanton numbers for various reaction orders and dimensionless rate constants. The effect of decreasing the reaction orders (from 2 to 1.5 to 1) is a substantial increase in the transfer coefficient. The increase from $n = 1.5$ to 1 is far in excess of that from $n = 2$ to 1.5. This is understandable because a decrease in the reaction order, with the rate constant remaining unchanged, causes an increase in the rate of depletion of the solute. This increases the concentration gradients at the interface, resulting in higher Stanton numbers [Equation (10)]. A similar increase in Stanton numbers is caused by increasing the value of the dimensionless reaction rate constant.

Wasan and Wilke (*16*) pointed out that for pure mass transfer the Stanton numbers approach a constant value for x^* between 12 to 15; this analysis very closely substantiates their results for changes in N_{St} as a function of x^*. With the occurrence of a chemical reaction there is a finite decrease in the length x^* required to achieve constant Stanton numbers. For a first order reaction with $K = 1$, the required length for 95% of fully developed conditions is about $x^* = 4$.

Figure 2 illustrates the effect of reaction orders on Stanton numbers for varying Schmidt numbers. An increase of Stanton numbers, with a decrease in reaction orders, is shown for every value of Schmidt number. Over the entire range, as N_{Sc} increases N_{St} progressively decreases. However, with an increase of N_{Sc} there is a gradual degree of divergence for transport numbers with chemical reaction, this divergence being greater as the reaction order decreases. We mentioned earlier that the transfer coefficients are enhanced by a chemical reaction occurring near the wall due to an increase in the concentration gradients. This effect is more apparent for higher values of N_{Sc} where the rate of change of the concentration gradients, in a correspondingly thinner wall region, is more rapid as a function of the reaction order.

Figure 3 shows the change in Stanton numbers as a function of Reynolds numbers for various reaction orders. The entire family of lines is almost linear. For pure mass transfer the slopes indicate a value of -0.20 over this range of Reynolds numbers. The value of the slope changes with a decrease in the reaction order until it attains a value of -0.30 for a first order reaction. The slow convergence with increasing Reynolds numbers is due to the decreasing effect of the reaction order in the wall region which is thinning out.

Veith, Porter, and Sherwood (*14*) in their analysis of a first order reaction show the increase in the transfer coefficient k_g/k^*_g as a function of $\sqrt{m} = \sqrt{k_n D/k^*_g}$, where k^*_g

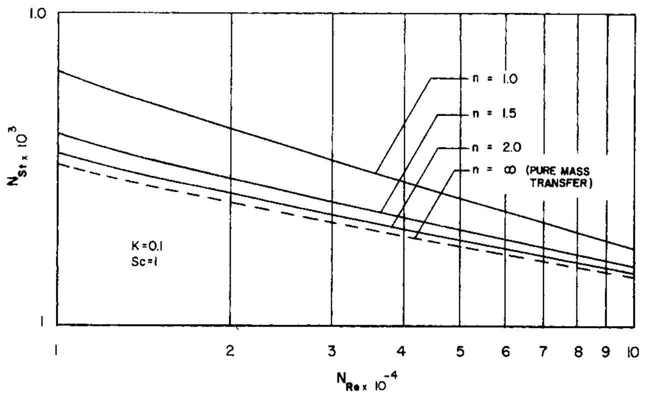

Fig. 3. Effect of reaction orders on Stanton numbers for varying Reynolds numbers.

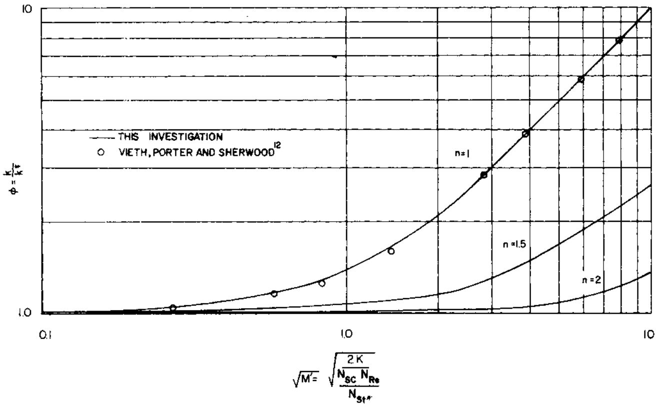

Fig. 4. Increase of transfer coefficients as a function of $\sqrt{m'}$ for different reaction orders.

is the mass transfer coefficient in the absence of the chemical reaction. A similar relation can be constructed for an arbitrary-order reaction by defining an $\sqrt{m'}$ of a more general character.

Define

$$\sqrt{m\rho^{n-1}} = \sqrt{m'} = \frac{\sqrt{\dfrac{2K}{N_{Re}N_{Sc}}}}{N_{St*}}$$

and

$$\varphi = \frac{k_g}{k^*_g} = \frac{N_{St}}{N_{St*}} \tag{11}$$

For a first order reaction $\rho^{n-1} = 1$

$$\sqrt{m} = \frac{\sqrt{\dfrac{2KU_{av}^2}{N_{Re}N_{Sc}}}}{N_{St*}\,U_{av}} = \frac{\sqrt{\dfrac{KU_{av}}{R}\cdot\dfrac{\nu}{N_{Sc}}}}{N_{St*}\,U_{av}} = \frac{\sqrt{k_nD}}{k^*_g}$$

Then $\sqrt{m'}$ reduces to $\sqrt{m}$ for a first order reaction, and $\sqrt{m'}$ as defined by Equation (11) can be used in the general analysis.

The results of the increase in the transfer coefficients for fully developed mass transfer with chemical reaction versus $\sqrt{m'}$, as defined by Equation (11), is shown in Figure 4. For a first order reaction the results are identical with those presented by Veith, Porter, and Sherwood (*14*). Beyond $\sqrt{m'} = 2$, as the reaction becomes more vigorous, φ slowly approaches $\sqrt{m'}$. For higher order reactions, as can be seen, there is a correspondingly slower increase in φ with respect to $\sqrt{m'}$. This is understandable from the results of our previous discussion. Care must be taken to remember that the results of Figure 4 are generally valid only for dilute reactive systems.

For first order reactions, the entry region's effect on the relation between φ and $\sqrt{m}$ is shown in Figure 5. There is a fairly rapid convergence towards fully developed values. However, for short transfer sections care must be taken in evaluating the coefficient ratio (φ). For a transfer section with $x^* = 0.025$, there is a 40 to 50% decrease in the transfer coefficient ratio φ as compared to those attainable under fully developed conditions.

Figure 6 illustrates the increase in average concentration for various reaction orders and dimensionless rate constants. The increase is maximum for $n \to \infty$ (no chemical reaction), whereas with a chemical reaction the reactant is consumed thereby decreasing the downstream concentration. For a first order reaction with $K = 1$ after $x^* \approx 2$, the reactant consumed is about equal to that being transferred into the flow stream, so that the downstream concentration remains unchanged.

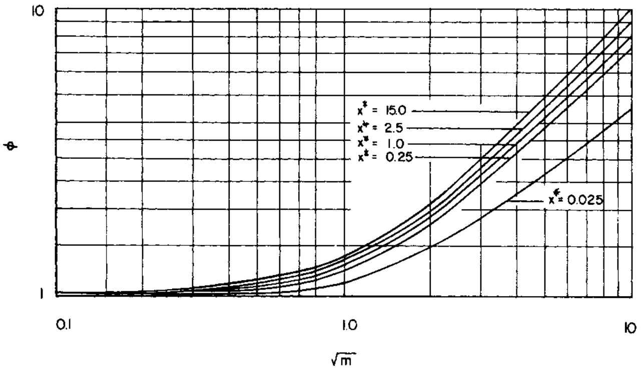

Fig. 5. Effect of entry region on relation between φ and $\sqrt{m}$.

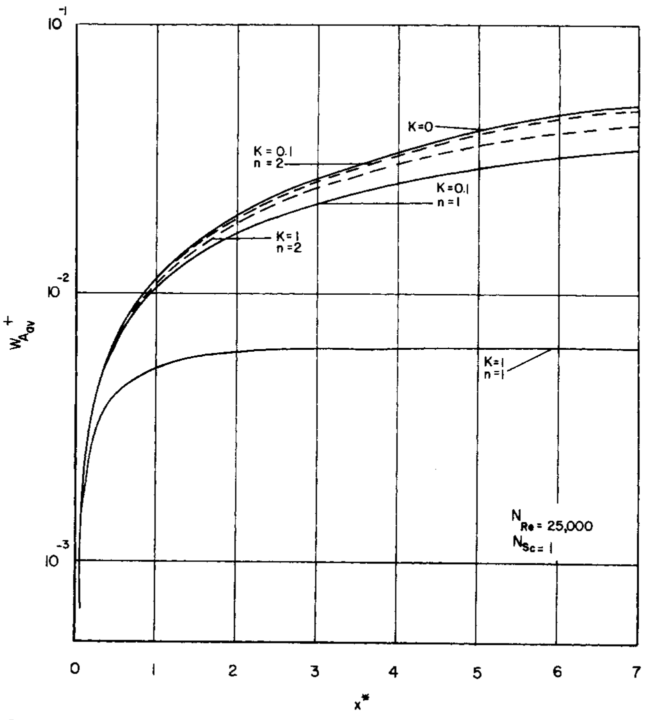

Fig. 6. Effect of various reaction orders and dimensionless rate constants on longitudinal average concentration distribution.

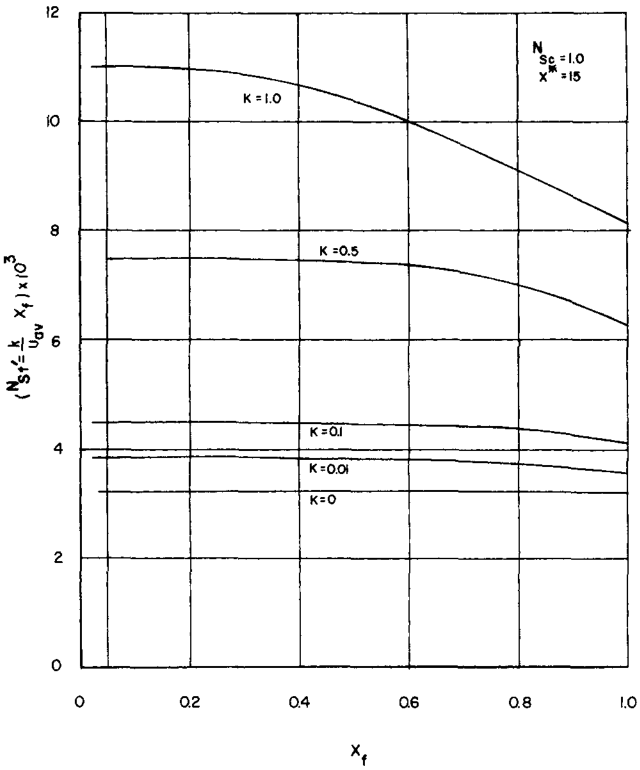

Fig. 7. Effect of film pressure factor on redefined Stanton numbers with and without chemical reaction ($N_{Sc} = 1$).

ROLE OF CONCENTRATION LEVELS

The magnitude of convective transport depends upon the concentration gradient of the solute as well as on that of the nondiffusing species. In the interpretation of gas phase mass transfer processes ($N_{Sc} \approx 1$) by molecular diffusion through a hypothetical stagnant film, the convective transport resulting from the diffusion process has usually been accounted for by the film pressure factor. For diffusion of one gas through a second stagnant gas, the film pressure factor becomes the log mean average concentration of the stagnant gas over the diffusion path. The role of log mean concentrations of nondiffusing species for pure mass transfer in a turbulent flow of gases ($N_{Sc} \approx 1$) was studied by Wasan and Wilke (*16*). We have extended this study to incorporate liquid systems ($N_{Sc} \approx 1000$) with and without a first order chemical reaction occurring between the solute and the solvent.

In order to establish the role of the film factor X_f in the gas and liquid phase processes, computed results have been expressed in Figures 7 and 8 on the basis of a Stanton number with the film pressure included. Results for mass transfer with no chemical reaction show that this Stanton number is constant over the range of X_f, indicating that the film factor enters to the first power. Note that the same relation also holds for $N_{Sc} = 1000$, a finding not reported by any previous investigator. With increasing rates of reaction, Stanton numbers become constant only for the lower range values of X_f. For liquid systems the approach toward constant Stanton numbers is much slower for comparative values of the rate constant.

The role of the film pressure factor in the entry region was also investigated. Mass transfer with and without chemical reaction was studied for the case of $x^* = 0.25$. Again within bounds, the result is identical to that exhibited for long transfer sections.

An increase in the ratio of Stanton numbers with and without chemical reactions (ϕ_{X_f}) as a function of the film pressure factor for $N_{Sc} = 1$ and 1000 was observed. In both cases, the effect of increasing the rate constants is an increase in the ratio of ϕ_{X_f} over the entire range of concentration levels. The effect of this increase is far more pronounced in systems having a higher Schmidt number (see Figure 9). There was a threefold increase in ϕ_{X_f} for a rate constant of $K = 1.0$ when the Schmidt number was changed from 1 to 1000. The effect of entry region has also been included in Figure 9. There is a continuous increase in ϕ_{X_f} as the transfer section increases, until steady state conditions are attained. This effect is also more pronounced in systems of higher Schmidt numbers.

CONCLUSIONS

The role of homogeneous chemical reactions on mass transfer in turbulent pipe flows was studied by using a numerical technique.

The Stanton numbers show an increase with an increase in the dimensionless rate constant or a decrease in the reaction order, or both. As the Schmidt numbers increase, the effect of the reaction order on the mass transfer coefficients also increases. With increasing Reynolds numbers, however, the effect of the reaction order decreases, indicating that at very high Reynolds numbers the effect of chemical reactions becomes negligible.

Good agreement was shown for first order reactions with the theory of Veith, Porter, and Sherwood. The results

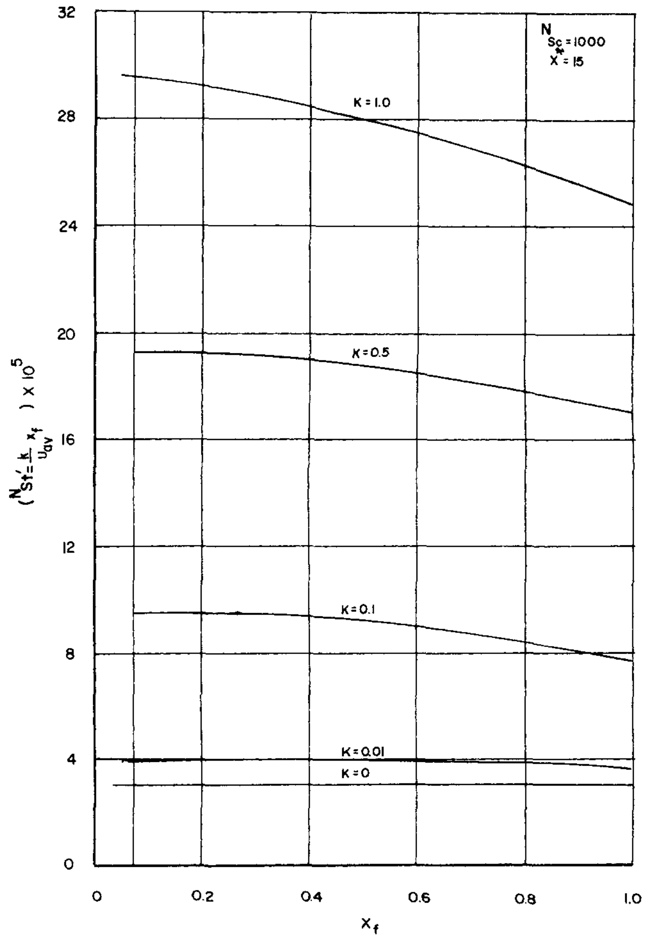

Fig. 8. Effect of film pressure factor on redefined Stanton numbers with and without chemical reaction ($N_{Sc} = 1000$).

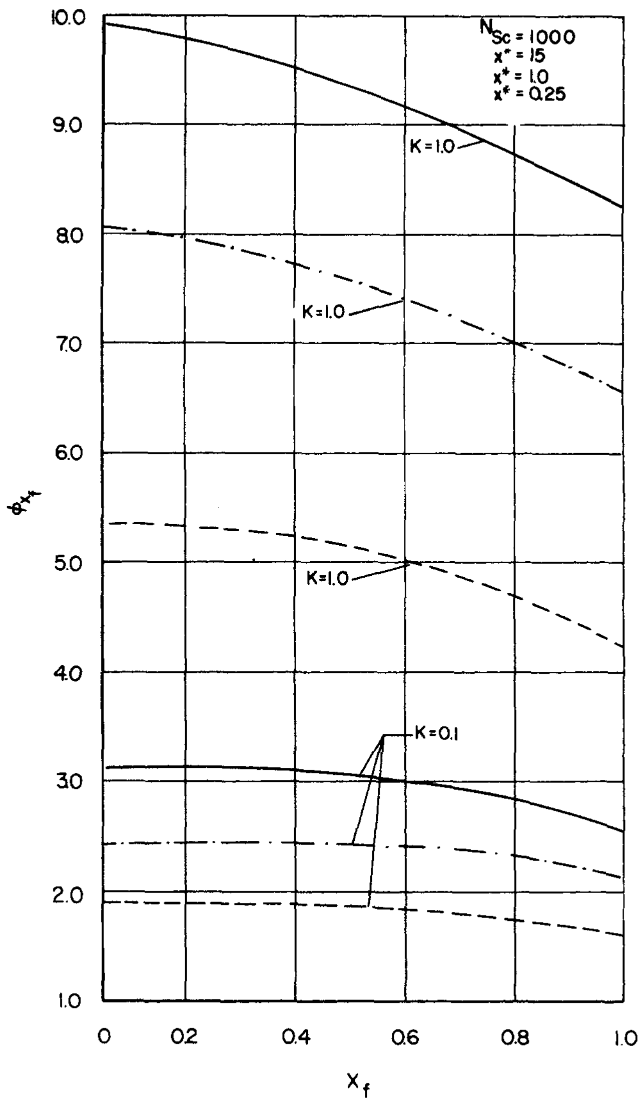

Fig. 9. Increase in ratio of Stanton numbers with chemical reaction to those without as a function of the film pressure factor for various aspect ratios ($N_{Sc} = 1000$).

were extended to arbitrary-order reactions as well as to the entry region. The effect of arbitrary reaction orders and rate constants on radial concentration profiles in the wall region was shown. Concentration levels' effects on mass transfer with chemical reactions for gaseous and liquid systems was studied. It was demonstrated that an increase in the concentration levels affects mass transfer. The ratio of transfer coefficients with a reaction to those without a reaction increases with an increase of Schmidt numbers and also with an increase in the length of the transfer section.

NOTATION

D = diffusion coefficient
E = eddy diffusion coefficient
k_g = mass transfer coefficient
k^*_g = mass transfer coefficient without chemical reaction
k_n = reaction rate constant
n = reaction order
N_B = flux of species B
r = radial coordinate
R = tube radius
R_A = homogeneous rate of reaction of species A
S = normalized transformed radial coordinate
S^+ = transformed radial coordinate
U = axial velocity
U_{av} = average axial velocity
U^* = dimensionless axial velocity, U/U_{av}
U^+ = dimensionless axial velocity, U/U_τ
U_τ = friction velocity, $\sqrt{\tau_w g_c/\rho}$
V = radial velocity
V_A = radial velocity of species A
V_B = radial velocity of species B
W_A = mass fraction of species A
W^+ = dimensionless mass fraction
W_B = mass fraction of species B
X_f = log mean fraction of nondiffusing species
x = axial coordinate
x^* = dimensionless axial coordinate, X/R
y = distance from pipe wall, $R - r$
y^* = dimensionless distance from pipe wall, y/R
y^+ = dimensionless distance from pipe wall, yU_τ/ν

Greek Letters

ϵ = eddy viscosity
μ = viscosity
ρ_t = total density of mixture
ρ_A = mass concentration of species A
ρ_B = mass concentration of species B
ν = kinematic viscosity, μ/ρ_t
τ_w = shear at the wall

Dimensionless Groups

N_{Re} = Reynolds number, $2R\ U_{av}/\nu$
N_{Sc} = Schmidt number, ν/D
N_{St} = Stanton number, k_g/U_{av}
N_{St^*} = Stanton number without chemical reaction, k_g^*/U_{av}
$N_{St'}$ = Stanton number with film pressure factor, $N_{St}\ X_f$

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