It has been shown previously that the first four of these derivatives are not numerically equal (Navari et al., 1971; Bryant and Navari, 1974), which leads to the conclusion that Equations (7) and (8) are, in turn, not equivalent. A recent paper (Goldstick et al., 1976) compares diffusion data by stating that $\partial f_5/\partial A)_{\alpha,\beta,\gamma}$ should be equal to df_3/dT. There is, clearly, no reason why this should be so. If one wishes to compare data for variations in diffusivity with changing total protein levels, one should account for the effect of each separate protein and its influence on the diffusion of oxygen. Goldstick et al. (1976) state that they found little difference using the total derivative rather than the partial derivatives in accounting for the protein effects on oxygen diffusivity in plasma. However, it is important to realize that each of the partial derivatives in Equation (7) are functions of the concentrations of the other proteins (those held constant during their evaluation). Values of these derivatives have been determined for one range of protein levels (the normal, average values for humans), and much of the data reported by Goldstick et al. (1976) are not for normal, average levels. This makes any comparison of previously obtained data quite difficult, if not impossible. This is compounded further by the fact that blood plasma taken from various hospital patients (Goldstick et al., 1976) is quite likely to contain drugs and medicines which could easily alter the diffusivity values obtained.

SUMMARY

As stated before, the diffusion of oxygen through plasma may prove to be important in physiological systems, and as more chemical engineers work in this area, care should be taken to realize that plasma is a solution containing many components. This makes any study concerning the concentration dependence of the diffusivity a multidimensional one. The assumptions that some variations are not important, or that the problem can be treated as being one dimensional, have not been proven, although many previous studies do not always appear to recognize this. In fact, the effects of drug levels in plasma on oxygen transport may be much more important, physiologically, than the effects of variations of protein levels, where almost all previous interest has centered. In summary, diffusion of oxygen through plasma may be affected by the concentrations of any of the constituents present normally in plasma, as well as those added (drugs), but no study made to date has considered this in detail. This may have also led to some misinterpretation of previous data. However, the experiments performed to date have established a foundation on which to build a future knowledge of this important system.

NOTATION

A = concentration of albumin in plasma
D_{O_2-P} = diffusivity of oxygen in plasma
F = concentration of fibrinogen in plasma
T = total protein level
α = concentration of α-globulin in plasma
β = concentration of β-globulin in plasma
γ = concentration of γ-globulin in plasma

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Large Schmidt Number Mass Transfer in Turbulent Pipe Flow

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Shaw and Hanratty (1977) have recently presented new, large Schmidt number data for fully developed turbulent mass transfer from a pipe wall. The electrochemical method was used, and the data, covering the range $693 \leq Sc \leq 37\,200$, appear to be of high precision. The authors found that the often assumed large Schmidt number relationship $St \propto Sc^{(1-n)/n}$, corresponding to $\epsilon^+ \propto y^{+n}$ near the wall, did not satisfactorily correlate their data for $n = 3$ or $n = 4$. The modified correlation proposed by Shaw and Hanratty for their data is

$$\frac{St}{\sqrt{f/2}} = 0.0889\, Sc^{-0.704} \qquad (1)$$

This expression was determined by fitting a function of the form $St/\sqrt{f/2} = CSc^a$, where C and a are free parameters. They report that a statistical calculation for their model shows that experimental errors could not account for the discrepancy between $a = -0.704$ and either $-2/3$ or $-3/4$. Heretofore, it has generally been accepted that $a = -2/3$ (Notter and Sleicher, 1971; Hanna and Sandall, 1972). The purpose of this note is to show that the large Sc asymptotic expansion of Hanna

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TABLE 1. RESULTS OF FITTING SHAW AND HANRATTY DATA

Equation	Mean dev. (%)	Standard dev. (%)
Equation (3) with three terms	2.21	3.07
Equation (3) with two terms ($C_3 = 0$)	2.24	3.07
Shaw and Hanratty correlation [Equation (1)]	2.33	3.08
Hughmark correlation [Equation (7)]	4.26	5.44

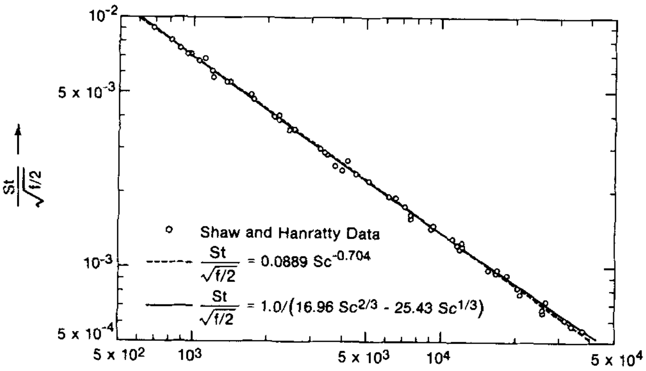

Fig. 1. Shaw and Hanratty data compared to correlation formulae.

and Sandall (1972) correlates the data as well as the semiempirical Equation (1), while retaining the usual $Sc \rightarrow \infty$ limit, $St/\sqrt{f/2} \propto Sc^{-2/3}$.

In our view, it is natural to suppose that the reason for the failure of the previous formula to adequately correlate the data for either $a = -2/3$ or $a = -3/4$ is that additional correction terms in the eddy diffusivity expression near the wall are needed in order to achieve the high accuracy which is warranted by the data. As shown in our earlier paper (Hanna and Sandall, 1972), inclusion of additional terms in the eddy diffusivity expansion near the wall, that is

$$\epsilon^+(y^+) = K_3 y^{+3} + K_4 y^{+4} + K_5 y^{+5} \tag{2}$$

leads to an asymptotic expansion for the Stanton number of the form shown in Equation (3), which is valid at large Schmidt numbers:

$$\frac{St}{\sqrt{f/2}} = \{C_1 Sc^{2/3} + C_2 Sc^{1/3} + C_3 \ln Sc + 0(1)\}^{-1} \tag{3}$$

This kind of expansion has successfully correlated non-Newtonian heat transfer results (Sandall, Hanna, and Gelibter, 1976) as well as earlier mass transfer data (Hanna and Sandall, 1972). Thus, it is conjectured that two or three terms of this large Schmidt number expansion should be appropriate for correlation of the Shaw and Hanratty data.

The C coefficients in Equation (3) are related to the K coefficients in the Taylor series expansion for ϵ^+, Equation (2). This result is for the uniform wall flux boundary condition; however, it was shown that for large Sc, the wall boundary condition has little influence on the St. An equation similar to Equation (3) was derived for the case corresponding to ϵ^+ beginning as y^{+4}.

The new Shaw and Hanratty data were fitted to Equation (3) using a nonlinear least-squares procedure to determine C_1, C_2, and C_3. The results of these calculations are shown in Table 1. The mean and standard deviations shown in Table 1 are defined as

$$\text{mean deviation} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{St_{\text{pred.}} - St_{\text{exp.}}}{St_{\text{exp.}}} \right|$$

standard deviation

$$= \left\{ \frac{1}{(N-P)} \sum_{i=1}^{N} \left(\frac{St_{\text{pred.}} - St_{\text{exp.}}}{St_{\text{exp.}}} \right)^2 \right\}^{1/2} \tag{5}$$

It was found that the precision of the data and the given Schmidt number range warrant the retention of C_1 and C_2, while the additional inclusion of C_3 does not improve the fit of Equation (3) to the data, indicating that the noise level of the data has been reached. Thus, the large Schmidt number correlation for the Stanton number based on our asymptotic formula is

$$\frac{St}{\sqrt{f/2}} = \{16.96\, Sc^{2/3} - 25.43\, Sc^{1/3}\}^{-1} \tag{6}$$

The case where ϵ^+ begins as y^{+4} was also considered, but, as in previous studies, it produced decidedly inferior results (standard deviation = 3.76%).

The entries of Table 1 show that Equation (6) fits the Shaw and Hanratty data slightly better than their correlation formula, Equation (1), with the result that St still varies as $Sc^{-2/3}$ for Sc sufficiently large. A correlation formula proposed by Hughmark (1977) for the Shaw and Hanratty data is also shown in the comparison. According to our calculations based on his formula and the Shaw (1976) data, the Hughmark formula provides a considerably less satisfactory fit of the data. The Hughmark formula is given by Equation (7):

$$\frac{St}{\sqrt{f/2}} = \left\{ \frac{1}{\dfrac{1}{1.6\, Sc} + 0.047\, Sc^{-2/3}} + \frac{1}{0.0615\, Sc^{-1/2}} \right\}^{-1} \tag{7}$$

Figure 1 shows the Shaw and Hanratty data compared to Equations (1) and (6). It is seen that both equations correlate the data well.

It is concluded that the calculations reported here show that the large Schmidt number asymptotic expansion of the customary formulation for turbulent mass transport, with $\epsilon^+ = K_3 y^{+3} + K_4 y^{+4}$ near the wall, agrees completely with the new data of Shaw and Hanratty.

NOTATION

C_1, C_2, C_3 = constants in Equation (3)
D = molecular diffusivity, m²/s
f = friction factor = $2\tau_w/\rho U_b^2$
k_c = mass transfer coefficient, m/s
K_3, K_4, K_5 = constants in Equation (2)
n = exponent on leading term in eddy diffusivity expansion
N = number of data points
P = number of fitted parameters
Sc = Schmidt number = ν/D
St = Stanton number = k_c/U_b
U_b = bulk velocity, m/s
u^* = friction velocity = $U_b\sqrt{f/2}$, m/s
y = distance measured from wall, m
y^+ = dimensionless $y = yu^*/\nu$
ν = kinematic viscosity, m²/s
ρ = density, kg/m³
τ_w = shear stress at the wall, kg/m s²

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Mathematical Models of the Monolith Catalytic Converter:

Part III. Hysteresis in Carbon Monoxide Reactor

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Hysteresis is examined for monolith chemical reactors that are used to oxidize carbon monoxide in automobile exhaust. The term hysteresis refers to a multiplicity of steady states, and the actual steady state depends on the past history of operation of the reactor. In particular, different outlet conversions are obtained for the same inlet temperature depending on whether the device starts out hot or cold. A model developed earlier (Young and Finlayson, 1976*a*, *b*) used the collocation method to solve the equations for heat, mass, and momentum transfer in a single adiabatic channel of the monolith. Here we examine the influence of several operating and design parameters on the earlier results: velocity, inlet concentration, geometry of the duct, thermal conductivity of the wall, and effective diffusivity in the porous layer. We then compare the model to experimental data.

MODEL

The basic model is the one described earlier (7, 8) as model II-A: a square duct with axial conduction longitudinally in the solid walls, but with infinitely fast conduction peripherally around the square, and including the diffusion of heat and mass in the transverse direction in the fluid. Nusselt and Sherwood numbers are not assigned a priori. The reaction rate expression is *P*2 in (8) with a basic form

$$\text{rate} = \frac{D y_{O_2} y_{CO} e^{-A/T}}{(1 + C' y_{CO} e^{B/T})^2} = \frac{k_o(E + y)y}{(1 + \alpha y)^2} \qquad (1)$$

This is the expression derived by Voltz et al. (1973) to fit their data. Here, however, we allow diffusion limitations in the very thin catalytic layer. The temperature is assumed constant within the layer since the primary heat transfer resistance occurs in the fluid. The effectiveness factor curve is generated using a one-term collocation for small Thiele modules and the asymptotic solution for large Thiele modules (Finlayson, 1974).

The diffusion in the catalytic layer is governed by

$$\begin{aligned} &D_s \frac{d^2c}{dx^2} = \text{rate}\,[c(x)] \\ &c = y_o c_o \quad \text{at} \quad x = \xi \qquad (2) \\ &\frac{dc}{dx} = 0 \quad \text{at} \quad x = 0 \end{aligned}$$

By introducing $c = yc_o$, with y the mole fraction carbon dioxide, and setting $y_{O_2} = (E + y)2/3$ (with $E = 0.03$, assuming y_{CO}/y_{H_2} remains constant), we can nondimensionalize this equation to give

$$\begin{aligned} &\frac{d^2y}{ds^2} = \phi^2 f(y) \\ &y = y_o \quad \text{at} \quad s = 1 \qquad (3) \\ &\frac{dy}{ds} = 0 \quad \text{at} \quad s = 0 \end{aligned}$$

$$\phi^2 = \frac{\xi^2 k_o g(y_o)}{D_s C_o}, \quad f(y) = \frac{g(y)}{g(y_o)} \qquad (4)$$

with

$$g(y) = \frac{(E + y)y}{(1 + \alpha y)^2} \qquad (5)$$

The asyptotic solution is

$$\begin{aligned} \eta &= \frac{\sqrt{2}}{\phi}\left[\int_o^{y_o} f(y)dy^{\;1/2}\right] \\ &= \frac{\sqrt{2}}{\phi}\,\frac{1}{g(y_o)}\left\{\frac{E}{\alpha^2}\left[\frac{1}{1 + \alpha y} + \log_e(1 + \alpha y)\right]\right. \\ &\left.+ \frac{1}{\alpha^3}\left[1 + \alpha y - 2\log_e(1 + \alpha y) - \frac{1}{1 + \alpha y}\right]\right\}_o^{y_o} \qquad (6) \end{aligned}$$

The reader desiring other details of the model is referred to Young & Finlayson (1967*a*, *b*).

PARAMETRIC STUDY

The hysteresis effect is illustrated in Figure 1. Such curves have been obtained experimentally by Hlaváček and Votruba (1974) and Mosterky et al. (1974) in the following manner. Beginning with a cold reactor, desired inlet conditions are maintained at a low temperature until steady state has been reached, giving one data point on

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