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Manuscript received July 14, 1975; revision received September 23, and accepted September 29, 1975.

Transport Through a Growing Boundary Layer to a Permeable Wall

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Boundary layer techniques are commonly used to describe the transport of heat or mass[*] in flowing systems. For fully developed steady flow through a pipe of uniform cross section, the shear rate at the pipe wall is uniform and constant (U/C), and boundary layer solutions are available [for example, Bird et al., (1960)] for wall flux when the U/C concentration at the wall is specified and for wall concentration when the U/C wall flux is given. Steady state solutions are also available for these boundary conditions of the first and second kind for the cases in which nonuniform concentration or flux profiles are specified, or when wall shear varies spatially (Lighthill, 1950; Chambre and Acrivos, 1956; Acrivos and Chambre, 1957; Friedman and Ehrlich, 1975; Ehrlich and Friedman, 1976).

If the flow is past a surface which is permeable to the solute, then the interface boundary condition is more complex and the variation along the wall of interfacial concentration or flux must in general be found by iterative numerical techniques (Friedman and Ehrlich, 1975; Ehrlich and Friedman, 1976). For the case of U/C shear and a radiation boundary condition (Carslaw and Jaeger, 1959), an explicit solution for C_w and g can be found; the purpose of this note is to present and discuss it.

ANALYSIS

It is easiest to begin with Lighthill's (1950) Equation (26), which relates the Laplace transforms of heat flux and wall temperature under a thermal boundary layer in a longitudinally varying shear field. Translated into mass transfer variables, his equation is

$$2^{1/2} L\left\{\frac{\overline{G}(t)}{\overline{S}^{1/2}(t)}\right\} = -\alpha p^{1/3} L\{\chi(t)\} \tag{1}$$

where $\overline{G}$, $\overline{S}$, and χ are defined on the independent variable

$$t = \frac{2^{1/2}}{Pe'}\int_0^{\overline{x}} \Omega_w^{1/2}(\overline{x}')\,d\overline{x}',\ \alpha = (2/3)^{2/3}\Gamma(2/3)/\Gamma(4/3),$$

and p is the Laplace variable. In deriving Equation (1), the nondimensional concentrations in the free stream and upstream of the concentration boundary layer ($\overline{x} < 0$) were set at zero.

In dimensional terms, the boundary condition for radiation into a medium at zero concentration (Carslaw and Jaeger, 1959) at the wall is $g = kC_w$. In nondimensional terms, $\overline{G}(t) = Sh \cdot \chi_1(t)$. Note that the upstream value of χ is zero, while that of χ_1 is unity ($C_w = C_o$); thus, for this problem, where the governing differential equation is linear in the derivatives of concentration, $\chi_1 = 1 + \chi$. When the nondimensional wall shear is uniformly Ω_w and the transforms of $\overline{G}(t)$ and $\chi(t)$ in Equation (1) are replaced by those of the corresponding functions of $\chi_1(t)$, one finds

$$L\{\chi_1(t)\} = \frac{1}{cp^{2/3} + p}$$

where $c = 2^{1/2} \cdot Sh/(\Omega_w^{1/2}\alpha)$.

The transform has a branch point at the origin. The inversion theorem is employed to find $\chi_1(t)$ by using a branch cut along the negative real axis:

$$\chi_1(t) = \frac{3^{1/2}c}{2\pi}\int_0^\infty \frac{\exp(-tx')}{(x')^{4/3} + cx' + c^2(x')^{2/3}}\,dx'$$

For the uniform shear case considered here, the independent variable t can be replaced by $(2\Omega_w)^{1/2}\overline{x}/Pe'$. By replacing the dummy variable x' by c^3z^3, where z is a new dummy variable, the reduced interfacial concentration defined on $\overline{x}$ is given by

$$\overline{C}_w(\overline{x}) = \frac{3^{3/2}}{2\pi}\int_0^\infty \frac{\exp(-b\gamma z^3)}{z^2 + z + 1}\,dz \tag{2}$$

where $b = [\Gamma(1/3)/\Gamma(2/3)]^3/3 = 2.58$ and $\gamma = Sh^3 \cdot \overline{x}/$

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[*] This research was initiated to address a problem related to solute transport in arteries and will be phrased in terms of mass transfer variables. The extension to other scalars is trivial.

$(\Omega_w Pe')$. At $\overline{x} = 0$, $\overline{C}_w = 1$; $\overline{C}_w$ then decreases monotonically as $\overline{x}$ increases.

DISCUSSION

The reduced wall concentration is concisely expressed in terms of a single dimensionless group γ, which in terms of dimensional variables equals $k^3x/(D^2S)$. The variation of $\overline{C}_w$ with γ is presented in Figure 1. For any problem of interest satisfying the assumptions leading to Equation (2), the value of γ is an a priori measure of the relative extents to which the fluid phase and interface resistances control the transport rate at the wall. When γ is large, the former resistance dominates and $\overline{C}_w \rightarrow 0$; when γ is small, transport is controlled by the interfacial permeability and $\overline{C}_w \rightarrow 1$.

The behavior of the solution near the limits of γ can be seen more clearly by expanding the transform of χ_1 in descending and ascending powers of p to give asymptotic expressions for $\overline{C}_w$:

$$\overline{C}_w = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n\, b^{n/3}}{\Gamma\left(1+\frac{n}{3}\right)}\, \gamma^{n/3} \quad (\gamma \text{ small}) \quad (3a)$$

$$\overline{C}_w = \frac{3^{1/3}}{\Gamma\left(\frac{1}{3}\right)}\gamma^{-1/3} - \frac{3^{2/3}\left[\Gamma\left(\frac{2}{3}\right)\right]^2}{\left[\Gamma\left(\frac{1}{3}\right)\right]^3}\gamma^{-2/3} - 0(\gamma^{-4/3}) + \ldots \quad (\gamma \text{ large}) \quad (3b)$$

The *first two* terms of Equation (3*a*) and the first term of (3*b*) are plotted in Figure 1. When γ is small and the interfacial resistance dominates, the asymptotic solution in Figure 1 is the solution for the uniform flux boundary condition; when γ is large and fluid phase resistance dominates, the flux obtained by multiplying the first term in Equation (3*b*) by the Sherwood number is the solution for the uniform concentration boundary condition $\overline{C}_w = 0(\overline{x} > 0)$. The full solution (2) must be used for intermediate values of γ.

APPLICATIONS

The use of Equation (2) to predict C_w or g at a location x, when the independent variables C_o, k, D, and S are known, is straightforward. Equation (2) can also be used to obtain interfacial permeability from wall flux measurements $g(x)$ under a growing concentration boundary layer in the following fashion. Use Equation (2) to construct a new function $\Phi(\gamma) = \gamma\overline{C}_w^3$. This function increases monotonically with γ. By recalling that $g = kC_w$, it can be seen that $\Phi = [g/C_o]^3\,[x/(D^2S)]$. If the terms on the right-hand side of this equation are known, Φ and hence γ can be found; then k is computed from the definition of γ: $k = (D^2S\gamma/x)^{1/3}$.

This technique was used (Friedman, 1976) to analyze Caro's (1974) measurements of the in vitro uptake of ^{14}C-4-cholesterol from serum flowing at a constant rate through canine common carotid arteries. Caro's largest experimental Φ was found to be 2.70×10^{-7}, and the corresponding largest γ was 2.78×10^{-7}. Hence, transport was seen to be controlled essentially entirely by the resistance at the interface, such that k was essentially identical to the (Friedman, 1976).

From the definition of γ, it can be seen that the nature of the solute affects the relative importance of the boundary layer and interfacial resistances through the ratio $Sh^3/Pe' \propto k^3/D^2$. The value of this ratio for oxygen diffusing into arteries from plasma is estimated to be 3×10^5 times that for cholesterol; hence calculations of oxygen transport in arteries (Friedman and Ehrlich, 1975) evince a considerable dependence of wall flux on boundary layer thickness, while similar calculations for cholesterol do not (Friedman, 1976).

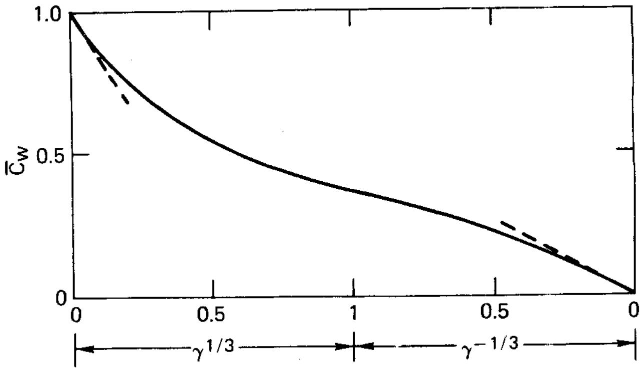

Fig. 1. Variation of reduced interfacial concentration $\overline{C}_w$ with nondimensional distance $\gamma = k^3x/(D^2S)$ downstream from the origin of the concentration boundary layer. Note that the function of γ on the abscissa changes from $\gamma^{1/3}$ to $\gamma^{-1/3}$ at $\gamma = 1$. The dashed lines are asymptotic solutions corresponding to the rate limiting resistance being in the fluid phase (γ large) or at the interface (γ small).

ACKNOWLEDGMENT

I am grateful to L. W. Ehrlich for helpful discussions and essential calculations. The investigation was supported by U.S. Public Health Service Grant 5P17HL14207.

NOTATION

C_o = solute concentration at the inlet
C_w = solute concentration at the wall
$\overline{C}_w$ = reduced solute concentration at the wall = C_w/C_o
D = solute diffusivity
$\overline{G}$ = nondimensional flux to the wall, defined on t; $\overline{G} = Lg/(DC_o)$
g = flux to the wall
k = interfacial permeability
L = characteristic length (for example, internal radius of a pipe)
Pe' = Peclet number for mass transfer = UL/D
Re = Reynolds number of the flow = UL/ν
S = shear rate = τ_w/μ
$\overline{S}$ = nondimensional wall shear, defined on t
Sh = Sherwood number = kL/D
t = independent variable defined below Equation (1)
U = mean inlet flow velocity
x = distance downstream from the origin of the concentration boundary layer
$\overline{x}$ = nondimensional distance downstream from the origin of the concentration boundary layer = x/L

Greek Letters

μ = fluid viscosity
ν = fluid kinematic viscosity = μ/ρ
ρ = fluid density
τ_w = wall shear
χ = nondimensional solute concentration at the wall, defined on t
χ_1 = reduced solute concentration at the wall, defined on t; $\chi_1 = C_w/C_o$
Ω_w = nondimensional wall shear = $L^2\rho\tau_w/(\mu^2 Re)$

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Manuscript received November 6, 1975; revision received December 29, and accepted December 30, 1975.

A Comparison of Enthalpy Prediction Methods

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A reliable method for estimating the liquid and vapor phase enthalpies of hydrocarbon mixtures is of critical importance in many calculations encountered in the petroleum and chemical industries. In the past 5 or 6 yr., a number of promising generalized correlations have appeared in the literature, several in the *Journal*. An extensive study, over a period of 5 yr., to evaluate the relative merits of these methods has now been completed. This work was carried out primarily to provide the basis for selecting the methods to be recommended in the Third Edition of the API Technical Data Book, Petroleum Refining (1976). A concise summary of this work is presented here.

The enthalpy prediction methods chosen for detailed evaluation were:

1. The Curl-Pitzer Tables (1958) using the molar average of the pure component critical points for the pseudocritical temperatures and pressures as suggested by Kay (1936).
2. The Curl-Pitzer Tables using the pseudocritical rules defined by Stewart, Burkhart, and Voo (1959). (These pseudocritical equations are hereafter referred to as the SBV rules.)
3. The equation of state given by Lee, Erbar, and Edmister (1973).
4. The Soave modification (1972) of the Redlich-Kwong equation of state.
5. Starling's (1971) modification of the BWR equation.
6. The Lee and Kesler (1975) three parameter corresponding states correlation.

Other correlations that were included in preliminary evaluations but which are not discussed in this paper were the Redlich-Kwong-Wilson equation (1966), the Hirschfelder et al. equation (1958), the Powers generalized correlation (Furtado et al., 1970), the Fisher-Leland corresponding states correlation (1970), and the Johnson-Colver two fluid method (1970). The six methods included in the final detailed evaluation were chosen on the basis of their generality or superior accuracy, based on the preliminary testing.

THE DATA

These six methods were tested against a data set consisting of 5 632 experimentally determined values. This set comprised sixteen single components, fifty-six binary mixtures, and six ternary mixtures. Except for pure nitrogen and the nitrogen-methane system, all data were for hydrocarbon systems. Only data derived from direct calorimetric determinations were used in the evaluations. More than 85% of the data were taken from the projects sponsored by the American Petroleum Institute and carried out by Lenoir and co-workers. References for these data are given in the supplement to this paper.*

The data set was classified into two categories. The first category consisted of those systems for which the actual experimental values were available. This set was comprised entirely of the data of Lenoir and co-workers. The second category consisted of those systems for which only smoothed values were reported by the authors. One would expect higher average deviations with the first category of data, since the random experimental errors have not been averaged out. The smoothing of the data, however, provides possibilities for biasing of the data. Table 1 gives a listing of the systems in the two categories.

In all cases, the data were represented in the form of enthalpy departures from the ideal gas values. Only single phase experimental points were used, since inclusion of two phase points would necessitate knowledge of the composition of each phase, data which were generally not available. All the data were plotted to confirm their assignments to the liquid or vapor phase. It was thus assured that the data set formed a consistent basis for comparison of the different methods. The critical properties and acentric factors needed for the evaluation were taken from the Second Edition of the API Technical Data Book, Petroleum Refining.

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* Supplementary material has been deposited as Document No. 02734 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.