Computer Simulation of Turbulent Mass Transfer at a Mobile Interface

Numerical solutions to the unaveraged mass balance equation for the case of a flat mobile interface reveal that both high- and low-frequency velocity fluctuations can contribute to mass transfer. This is in contrast to transport to a solid boundary where only low-frequency fluctuations, normal to the wall, are important. The average mass transfer coefficient is found to depend on Schmidt number to the -0.5 power, in agreement with classical theories. It is related to the velocity field in the liquid primarily through the mean-square value of the gradient of normal velocity fluctuations at the interface.

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SCOPE

The absorption of a slightly soluble gas in a concurrent, turbulent gas-liquid flow is controlled by flow fluctuations in the liquid through mechanisms that are not yet understood. This is a situation where the Schmidt number is large, and as a consequence the concentration boundary layer in the liquid is confined to a very thin region near the interface. Shear, caused by the gas flow, induces wave formation and also greatly enhances mass transfer rates. Mass transfer coefficients measured by Aisa et al. (1981) and McCready and Hanratty (1984b) are about one order of magnitude larger than those found for turbulent mass transfer at a solid boundary. The fundamental problem that must be considered in order to understand mass transfer in these complex flows is how the gas and liquid velocity fields interact to control the transport rate. The work presented here addresses this question by numerically solving the unaveraged mass balance equations for a randomly varying velocity.

A similar approach was taken previously by Campbell and Hanratty (1983) in their studies of mass transfer between a turbulent fluid and a solid boundary. These yielded the surprising result that mass transfer is controlled by low-frequency velocity fluctuations normal to the surface that contain only a small fraction of the turbulent energy.

The principal hydrodynamic difference between the case considered here and the case considered by Campbell and Hanratty is that near a mobile boundary the velocity normal to the boundary varies linearly with distance from the boundary, rather than quadratically. The goal of this work has been to explore the consequences of this difference.

CONCLUSIONS AND SIGNIFICANCE

Mass transfer at a mobile boundary (a clean gas-liquid interface) is found to be fundamentally different from mass transfer at an immobile boundary (a contaminated gas-liquid interface or a solid), in that velocity fluctuations of all frequencies are playing an important role. This is reflected in the equations for the mass transfer coefficient that are derived from computer experiments.

The velocity normal to mobile and immobile surfaces are given respectively by $v = \beta(x, z, t)\, y$, and $v = \beta(x, z, t)\, y^2$, where all terms have been made dimensionless using a friction velocity and the kinematic viscosity. Campbell and Hanratty (1983) derived the following equation for the dimensionless mass transfer coeffi-

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cient, $\overline{K}$, for an immobile boundary: $\overline{K}\,S^{0.7} = 0.09\,(W_\beta(0)/0.01)^{0.21}$, where $W_\beta(0)$ is the spectral density function of β^2 evaluated at zero frequency. For a mobile interface we find that $\overline{K}$ is primarily dependent on $\overline{\beta^2}$ and not on $W_\beta(0)$. The following approximate equation is derived: $\overline{K}\,S^{0.5} = 0.71\,(\overline{\beta^2})^{1/4}$, with $\overline{\beta^2} = \int_0^\infty W_\beta(\omega)\,d\omega$. The importance of this result is that it defines the rate of mass transfer in terms of a well-defined property of the fluctuating velocity field. This provides a way to evaluate proposed mechanisms of mass transfer.

Background

In concurrent gas-liquid flows, mass transfer occurs across an interface that is usually covered with three-dimensional waves of various frequencies and wavelengths. However, because the concentration boundary layer is very thin, the curvature of the surface should not directly affect the transport rates. Consequently, these flows are modeled as having a flat interface, with velocity fluctuations resulting from waves and turbulence in the gas or liquid. The concentration and velocity fluctuations are taken as two-dimensional. Derivatives of the concentration in the flow direction are neglected since it is expected that fluctuations in the flow direction are greatly elongated. This is the same description used by Campbell and Hanratty (1983) for turbulent transport near a solid boundary. Consequently a direct comparison with the results of their computer experiments on mass transfer to a solid boundary is possible.

The behavior of turbulent mass transfer near a solid boundary has been characterized experimentally by Sirkar and Hanratty (1970), Shaw and Hanratty (1977), and Campbell and Hanratty (1983). These measurements indicate that the scale of concentration fluctuations is similar to that for the velocity fluctuations and that the mass transfer fluctuations have a much lower frequency than the velocity fluctuations. In addition, Shaw found that the mass transfer coefficient varies with Schmidt number to the -0.7 power, in contradiction to classical theories.

Brodkey et al. (1978) presented the first numerical solution to a form of the unaveraged mass balance equation for transfer near a solid boundary. This solution does not represent a fully developed turbulent flow because an unrealistic velocity input, discontinuous in time and having a linear variation of normal velocity with distance from the wall, was used.

Campbell and Hanratty (1983) solved a two-dimensional form of the nonlinear mass balance equation using a measured velocity gradient signal. They were able to calculate accurately the magnitude of the average and fluctuating mass transfer coefficients, as well as the -0.7 power variation with Schmidt number. In addition, they found that very low frequency normal velocity fluctuations control the mass transfer rate. The importance of low-frequency fluctuations is also suggested by the analytical solution to a one-dimensional linearized mass balance equation given by Sirkar and Hanratty (1970).

A linearized mass balance equation that is valid near a mobile interface was solved by McCready and Hanratty (1984a). This solution does not exhibit the strong damping of high frequencies at large Schmidt numbers that is found at a fixed interface. Consequently, this suggests that higher frequency fluctuations will be relatively more important at a mobile interface than at a solid boundary. The calculations presented here will support this prediction and point to fundamental differences between transfer at mobile and fixed interfaces.

Theory

General equations

The equation that governs mass transfer at an interface is

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + V\frac{\partial C}{\partial y} + W\frac{\partial C}{\partial z} = \frac{1}{S}\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right), \quad (1)$$

where S is the Schmidt number, and U, V, and W are the velocities in the flow, x, the normal, y, and the transverse, z, directions. All terms have been made dimensionless using u^*, the interfacial friction velocity, ν, the kinematic viscosity, and the difference between the interfacial and the bulk concentration, $C_I - C_B$.

The Taylor expansions describing velocity in terms of distance from the interface are

$$U = \overline{U}(y) + \alpha(x, z, t) \quad (2)$$

$$v = \beta(x, z, t)\,y, \quad (3)$$

and

$$w = \gamma(x, z, t). \quad (4)$$

These equations satisfy the continuity equation and describe the velocity in the concentration boundary layer for large Schmidt numbers.

Linear equation

A simplified equation describing the fluctuating concentration, $c = C - \overline{C}$, is obtained if the concentration variation in the flow direction is neglected, if terms nonlinear in the fluctuating quantities are ignored, and if $(\partial^2 c/\partial z^2) \ll (\partial^2 c/\partial y^2)$ because of the thinness of the concentration boundary layer:

$$\frac{\partial c}{\partial t} + \beta y\frac{d\overline{C}}{dy} = \frac{1}{S}\frac{\partial^2 c}{\partial y^2}. \quad (5)$$

An analytic solution, presented by McCready and Hanratty (1984a), relates the spectral function for β, $W_\beta(\omega)$, defined as

$$\overline{\beta^2} = \int_0^\infty W_\beta(\omega)\,d\omega, \quad (6)$$

to the high-frequency portion of the spectral function for the

fluctuating mass transfer coefficient,

$$W_k(\omega) = \frac{W_\beta(\omega)\,\overline{K}^2}{\omega^2}. \tag{7}$$

This is similar to the corresponding solution for transport near a solid boundary, which Sirkar and Hanratty (1970) assumed to be valid for high-frequency mass transfer fluctuations:

$$W_k(\omega) = \frac{W_\beta(\omega)\,4\overline{K}^2}{\omega^3 S}. \tag{8}$$

In these equations ω is the dimensionless circular frequency, the average mass transfer coefficient $\overline{K}$ is defined as

$$\overline{K} = \frac{1}{S}\left.\frac{d\overline{C}}{dy}\right|_o, \tag{9}$$

and the fluctuating mass transfer coefficient, as

$$k = \frac{1}{S}\left.\frac{\partial c}{\partial y}\right|_o. \tag{10}$$

Equations 8 and 7 both predict that high-frequency velocity fluctuations are less effective in causing mass transfer fluctuations at the wall because of the appearance of the ω^2 and ω^3 terms in the denominators. However, it is noted that Eq. 8 predicts that a strong effect of Schmidt number on this filtering will be found at a solid surface. According to Eq. 8 a decrease in $W_k(\omega)$ is obtained with increasing Schmidt number, for a fixed frequency.

Scaling suggested by the linear equation

The full solution of Eq. 5, valid for both high- and low-frequency mass transfer fluctuations, is too cumbersome to obtain a physical understanding of the implications of linear theory regarding the mass transfer process. Consequently, an order-of-magnitude analysis of the type developed by Vassiliadou (1985) is presented here for the purpose of comparing linear theory predictions with solutions to the nonlinear equation described in the next section.

First consider solutions of Eq. 5 for high frequency and for high Schmidt number. Then $(\partial c/\partial t) \gg (1/S)\,(\partial^2 c/\partial y^2)$ except for a region $y < \delta_c$ close to the surface. For $y > \delta_c$,

$$\frac{\partial c}{\partial t} \sim \beta y \frac{d\overline{C}}{dy}. \tag{11}$$

Define a characteristic thickness of the concentration boundary layer as

$$\frac{1}{\delta} = \frac{d\overline{C}}{dy}. \tag{12}$$

It is expected that the magnitude of the concentration fluctuations, c' should be a maximum at $y \approx \delta$ and be zero at $y = 0$ and at very large y. Thus, from Eqs. 11 and 12 the magnitude of c' scales as indicated below:

$$c' \sim \frac{\beta}{\omega}. \tag{13}$$

Similarly, it is expected that the term characterizing turbulent transport also is a maximum roughly at $y = \delta$. Thus the magnitude of vc' scales as

$$vc' \sim \frac{\beta^2\delta}{\omega} \tag{14}$$

Molecular diffusion starts to affect the fluctuating concentration field at $y = \delta_c$, where

$$\frac{\partial c'}{\partial t} \sim \frac{1}{S}\frac{\partial^2 c'}{\partial y^2}. \tag{15}$$

From Eq. 15

$$\delta_c^2 = \frac{1}{\omega S}. \tag{16}$$

At $y = \delta_c$

$$c' \sim \frac{\beta\delta_c}{\omega}\frac{d\overline{C}}{dy}. \tag{17}$$

It follows that

$$\frac{k'}{\overline{\overline{K}}} \sim \frac{\beta}{\omega} \tag{18}$$

or that

$$W_k \sim \overline{K}^2\frac{W_\beta}{\omega^2}, \tag{19}$$

in agreement with Eq. 7.

For low enough frequencies that $(\partial c'/\partial t) \ll (1/S)\,(\partial^2 c'/\partial y^2)$, the magnitude of c' is estimated from the following relation

$$\frac{1}{S}\frac{\partial^2 c'}{\partial y^2} \sim v\frac{d\overline{C}}{dy}. \tag{20}$$

Thus from Eqs. 20 and 12 the magnitude of c' for low-frequency velocity fluctuations scales as follows:

$$c' \sim \beta\delta^2 S \tag{21}$$

Similarly

$$\frac{k'}{\overline{\overline{K}}} \sim \beta\delta^2 S \tag{22}$$

and

$$vc' \sim \beta^2\delta^3 S \tag{23}$$

for low-frequency velocity fluctuations.

Now, according to linear theory the different frequencies are acting independently; thus their contributions to vc' can be summed. This sum can be estimated by making the simplifying assumption that Eq. 14 is valid for $\omega < \omega_c$ and Eq. 23 is valid for

$\omega > \omega_c$, where ω_c is estimated from the relation that at $y = \delta$

$$\frac{\partial c'}{\partial t} \sim \frac{1}{S}\frac{\partial^2 c'}{\partial y^2}$$

or that

$$\omega_c = \frac{1}{\delta^2 S}. \tag{24}$$

Thus the Reynolds transport term scales as follows:

$$vc' = \int_0^{\omega_c} \delta^3 S\, W_\beta(\omega)\, d\omega + \int_{\omega_c}^{\infty} \delta \frac{W_\beta(\omega)}{\omega}\, d\omega \tag{25}$$

This can be rewritten as

$$vc' = \int_0^1 \delta\, W_\beta(\omega)\, d\frac{\omega}{\omega_c} + \int_1^\infty \delta \frac{W_\beta(\omega)}{(\omega/\omega_c)}\, d\left(\frac{\omega}{\omega_c}\right). \tag{26}$$

Now, since at $y = \delta$ turbulent transport is approximately equal to molecular transport,

$$vc' \sim \frac{1}{S}\frac{d\bar{C}}{dy}. \tag{27}$$

By equating Eqs. 26 and 27 the following relation for δ is obtained:

$$\delta^2 = S^{-1}\left[\int_0^1 W_\beta(\omega)\, d\left(\frac{\omega}{\omega_c}\right) + \int_1^\infty \frac{W_\beta(\omega)}{(\omega/\omega_c)}\, d\left(\frac{\omega}{\omega_c}\right)\right]^{-1} \tag{28}$$

Following Vassiliadou (1985) the spectral function is assumed to be of the form

$$W_\beta(\omega) = \frac{W_\beta(0)}{1 + \left(\frac{\omega\sigma}{\omega_m}\right)^2}, \tag{29}$$

where ω_m is the mean frequency,

$$\omega_m = \frac{\int_0^\infty \omega\, W_\beta(\omega)\, d\omega}{\int_0^\infty W_\beta(\omega)\, d\omega} \tag{30}$$

and σ is a shape factor,

$$\sigma = \omega_m \pi \frac{W_\beta(0)}{\overline{\beta^2}}. \tag{31}$$

The following scaling is then obtained by substituting Eq. 29 into Eq. 28:

$$\delta \sim S^{-1/2} W_\beta^{1/2}(0)\left\{\frac{\tan^{-1}\left(\frac{\sigma\,\omega_c}{\omega_m}\right)}{\left(\frac{\sigma\,\omega_c}{\omega_m}\right)} + \frac{1}{2}\ln\left(1 + \frac{\omega_m}{\sigma\omega_c}\right)^2\right\}^{-1/2} \tag{32}$$

It is clear that this scaling depends on the ratio of ω_c to ω_m, through

$$\frac{\sigma\,\omega_c}{\omega_m} = \frac{\pi\, W_\beta(0)\,\omega_c}{\overline{\beta^2}} \tag{33}$$

If Eq. 24 is substituted for ω_c and if $\bar{K}$ is assumed to scale as

$$\bar{K} = \frac{1}{\delta S} \tag{34}$$

then an estimate of the frequency ratio parameter is given as

$$\frac{\sigma\,\omega_c}{\omega_m} = \frac{\pi\, W_\beta(0)\,\bar{K}^2 S}{\overline{\beta^2}} \tag{35}$$

For large $\sigma\omega_c/\omega_m$ Eq. 32 simplifies to

$$\delta \sim S^{-1/2}(\overline{\beta^2})^{-1/4}. \tag{36}$$

It follows from Eqs. 35 and 34 that

$$\bar{K} \sim S^{-1/2}(\overline{\beta^2})^{1/4} \tag{37}$$

for large $\sigma\omega_c/\omega_m$.

In a similar way it can be shown that for small $\sigma\omega_c/\omega_m$, $\bar{K}$ depends only on $W_\beta(0)$,

$$\bar{K} \sim S^{-1/2} W_\beta^{1/2}(0) \tag{38}$$

For intermediate $\sigma\omega_c/\omega_m$, the mass transfer coefficient will depend both on $\overline{\beta^2}$ and on $W_\beta(0)$.

Nonlinear model

Since it is assumed that velocity changes in the flow direction are quite gradual, x-derivatives are neglected and Eq. 1 reduces to

$$\frac{\partial C}{\partial t} + \beta(z,t)\, y\frac{\partial C}{\partial y} + \gamma(z,t)\frac{\partial C}{\partial z} = \frac{1}{S}\left(\frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right). \tag{39}$$

At present, there is not enough experimental information to determine $\beta(z,t)$ and $\gamma(z,t)$ completely, so the simplified model suggested by Campbell and Hanratty (1983) has been used. The spatial variation of the velocity field is represented by a single harmonic, so that

$$\beta(z,t) = \sqrt{2}\,\beta(t)\cos(2\pi z/\lambda_z), \tag{40}$$

and

$$\gamma(z,t) = -\sqrt{2}\,\beta(t)\frac{\lambda_z}{2\pi}\sin\left(\frac{2\pi z}{\lambda_z}\right), \tag{41}$$

with $\beta(t)$ being a random function of time. The transverse wavelength, λ_z, was taken to be 100 for most of the calculations so as to agree with the measured behavior near a solid boundary. It is noted, however, that varying λ_z from 50 to 800 produced little effect on the calculated results.

The numerical solution of Eq. 39 using velocities described by Eqs. 40 and 41 required a time-varying signal to represent the normal velocity gradient at the interface. Experimental measurements of this gradient are not available for a mobile interface, so the time series measured by Lau (1980) at a solid boundary was used. The normalized power spectrum for this series is shown in Figure 1, with ω_m defined as the mean frequency. This is similar to the signal used by Campbell and Hanratty (1983) in their computer simulation of mass transfer at a solid boundary. However, the one used here contains more energy at high frequencies. Because the true behavior of the normal velocity fluctuations near a mobile interface is not known, the magnitude and median frequency of the input signal were varied. Thus, the basic assumption is that the shape of the spectral function, but not the median frequency nor the magnitude, characterizing the normal velocity fluctuations is the same at a gas-liquid boundary as at a liquid-solid boundary.

Numerical Methods

Equation 39 was solved using a finite-difference method that involved upwinding of the velocity terms (Roache, 1972). The boundary conditions used were $C = 0$ at $y = 0$, $C = 1$ at the outer boundary, for inflows, and $\partial C/\partial y = 0$ for outflows. These are the same conditions used by Campbell and Hanratty (1983) and they appear to be physically realistic.

Twenty-six grid points in the transverse direction, 33 grid points in the normal direction, and 8,000 steps in time were used in the calculations. Variations in the number of spatial or time steps appeared to have little effect on the results.

Results

Effect of the velocity gradient input signal

Measurements of gas absorption rates of O_2 into thick water layers presented by Aisa et al. (1981) and McCready and Hanratty (1985) suggest that $\overline{K}$, the dimensionless mass transfer coefficient, is constant at a value of approximately 0.009 for a Schmidt number of 440. Calculations were done to determine the value of $\overline{\beta^2}$ necessary to obtain these mass transfer coefficients. Figure 2 is a plot of $\overline{K}$ vs. $\overline{\beta^2}$ for various median frequencies. It is seen that median frequency has a weak effect. The median frequency measured near a solid boundary is about 0.088 and the largest value, 0.176, is approximately the characteristic frequency of the surface waves occurring in the gas-liquid flow experiments by McCready and Hanratty (1985). The value of $\overline{\beta^2}$ that corresponds to a mass transfer coefficient of 0.009 is about 10^{-2}

A comparison of the results shown in Figure 2 with Eq. 37 indicates that the relation derived for large $\sigma\omega_c/\delta_m$ appears to represent the calculations reasonably well.

Effect of $W_\beta(0)$

Campbell and Hanratty (1983) have identified the importance of $W_\beta(0)$, the energy contained in the very low frequency velocity fluctuations, in controlling mass transfer. In the calculation presented for constant ω_m in Figure 2 both $\overline{\beta^2}$ and $W_\beta(0)$ were increased at the same time. Therefore calculations were also carried out in which $W_\beta(0)$ and $\overline{\beta^2}$ were separately varied.

Figure 3 shows results in which $\overline{\beta^2}$ is kept constant at 0.0085 as $W_\beta(0)$ is varied. To do this ω_m was decreased as $W_\beta(0)$ was increased. It is noted from Eq. 35 that $W_\beta(0) = 0.1$ corresponds to $\sigma\omega_c/\omega_m \cong 3.9$ and that this parameter increases with increasing $W_\beta(0)$. This plot shows a slight decrease in $\overline{K}$ with $W_\beta(0)$ for $\sigma\omega_c/\omega_m < 3.9$. However, the influence of $W_\beta(0)$ on $\overline{K}$ for the range of parameters considered is much smaller than would be suggested from Eq. 38 for small $\sigma\omega_c/\omega_m$.

The dashed line in Figure 3 is the result obtained by Campbell and Hanratty for mass transfer to a solid boundary

$$\overline{K}\,S^{0.7} = 0.09\left(\frac{W_\beta(0)}{0.01}\right)^{0.21} \tag{42}$$

It is readily seen that calculated mass transfer rates are larger for a mobile interface than for a solid surface.

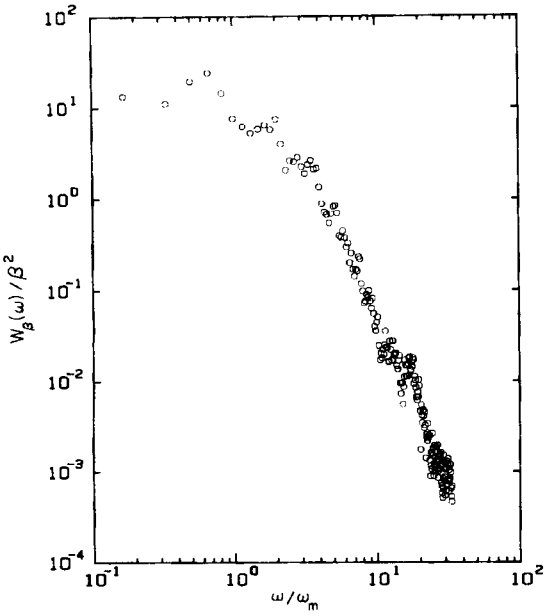

Figure 1. Power spectrum of the time-varying velocity signal used in the calculations.

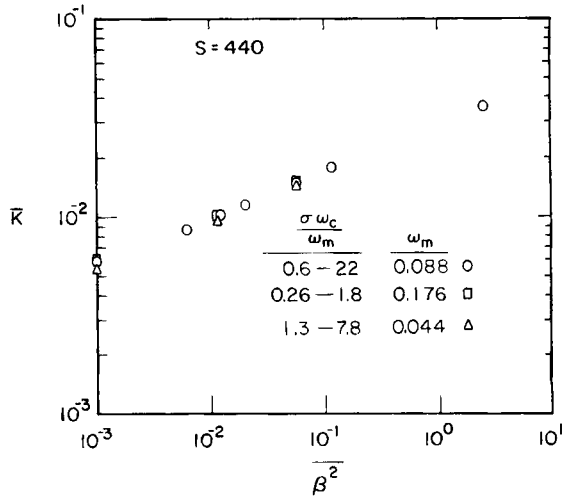

Figure 2. Effect of root-mean-square fluctuating velocity gradient on the average mass transfer coefficient.

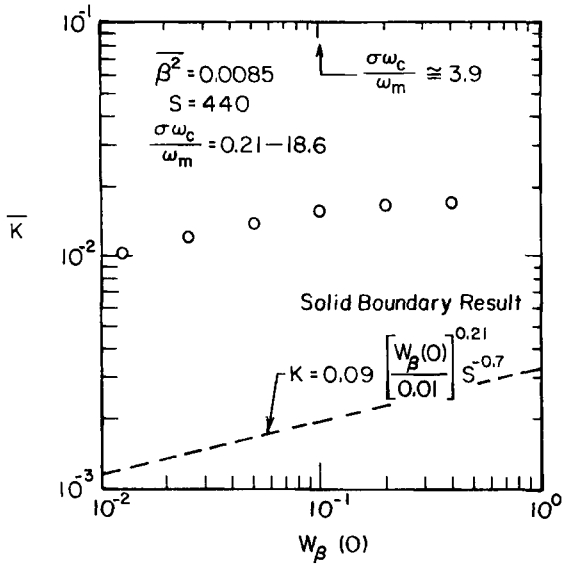

Figure 3. Effect of $W_\beta(0)$ on the mass transfer coefficient, with $\overline{\beta^2}$ held constant.

Comparison with the linear equation

Instantaneous mass transfer coefficients were calculated for each time step at each spatial step in the transverse direction. The mass transfer spectrum, which is a representation of these fluctuating mass transfer coefficients, will vary depending on the spatial location. As a result of this variation, a number of possible procedures exist for calculating spectra. For the work presented here, they are obtained from the instantaneous mass transfer coefficient at the seventh spatial step.

Spectra at both a mobile interface and at a solid boundary, obtained in this way, are shown in Figure 4. These spectra display the qualitative differences predicted by linear theory. For a solid boundary, where lower frequency velocity fluctuations contribute most to mass transfer, the median frequency is 0.002. At a mobile interface, the median frequency of the mass transfer spectrum is the same as for the velocity spectrum 0.088. No damping is occurring for this case. The curves shown in Figure 4 represent the spectra calculated from linear theory, Eqs. 7 and 8.

Figure 5 displays calculated normalized spectra for three different Schmidt numbers. It is seen that the Schmidt number affects the energy in the mass transfer spectrum only through $\overline{K}$, as predicted by Eq. 7, derived from linear theory. This is in contrast to what is found for mass transfer to a solid boundary (Shaw and Hanratty, 1977; Campbell and Hanratty, 1983).

Influence of Schmidt number on K

The calculated effect of the Schmidt number on the average mass transfer coefficient is shown in Figure 6. The result, which agrees with both the classic prediction of surface renewal theory and the linearized scaling presented earlier, is that $\overline{K}$ varies as $S^{0.5}$. The equation represented by the dashed line shown in Figure 6 and the results in Figure 2 is

$$\overline{K}\, S^{1/2} = 0.71\, (\overline{\beta^2})^{1/4}. \tag{43}$$

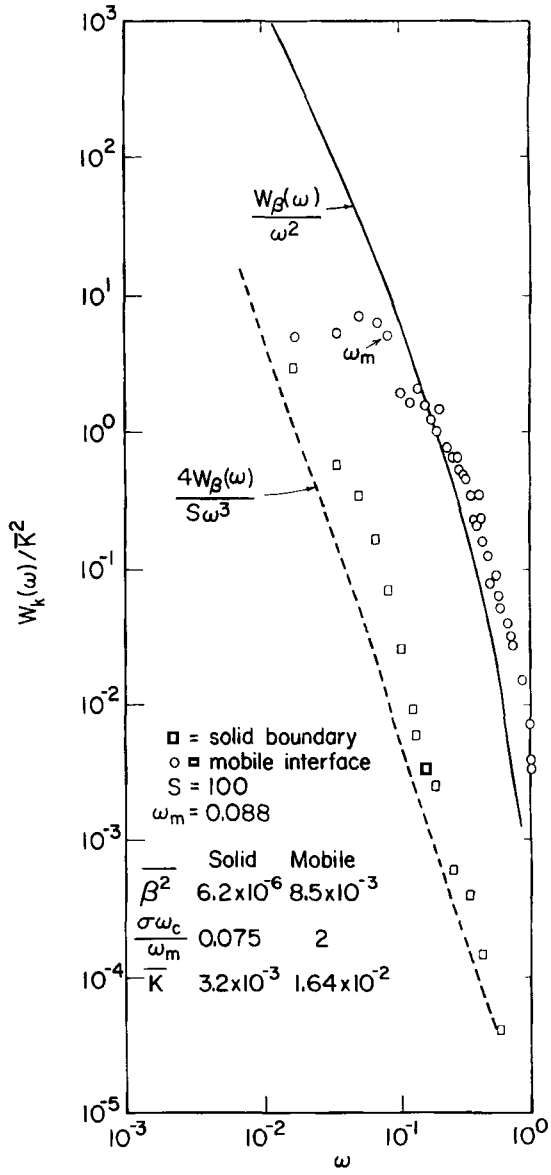

Figure 4. Comparison of the frequency spectra of the mass transfer fluctuations at a mobile boundary and a solid boundary.

Discussion

Linear theory scaling

As already pointed out by Vassiliadou, characteristic frequency ω_c, defined by Eq. 24, plays a critical role in understanding the relation of the fluctuating concentration field to the fluctuating velocity field. If the median frequency of the velocity fluctuations is much less than ω_c (large $\sigma\omega_c/\omega_m$), then the concentration field responds to all frequencies of the velocity field. This is a pseudosteady state approximation for which the term $\partial c/\partial t$ in the mass balance equation is playing a minor role. The concentration fluctuations are created by normal velocity fluctuations by the term $v\,(d\overline{C}/dy)$, and the magnitude of the concentration fluctuations is determined by

$$\frac{1}{S}\frac{\partial^2 c'}{\partial y^2} \sim v\frac{d\overline{C}}{dy}. \tag{44}$$

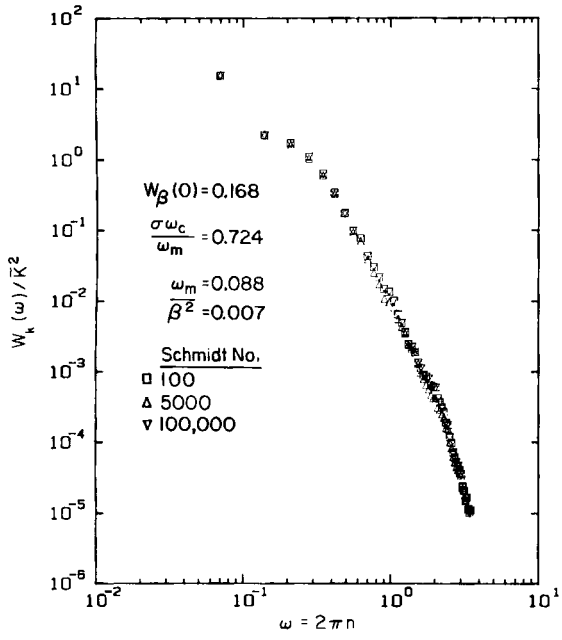

Figure 5. Effect of Schmidt number, results scaled according to linear theory.

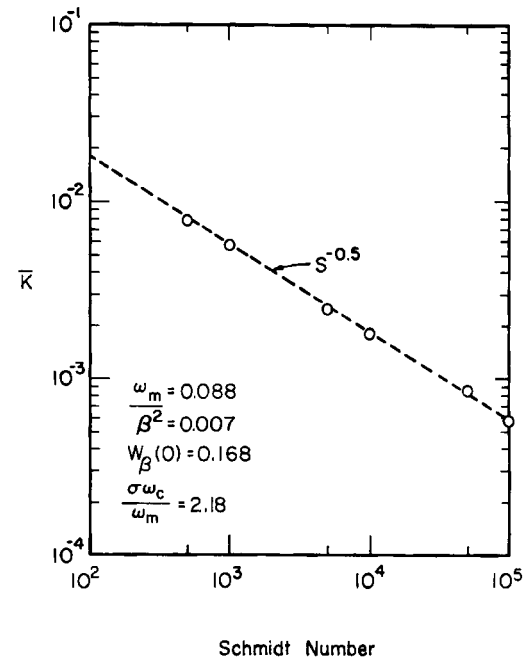

Figure 6. Computed effect of Schmidt number on the average mass transfer coefficient.

The average mass transfer coefficient is related to the entire energy of the velocity field, as given by Eq. 37.

If ω_c is much less than ω_m (small $\sigma\omega_c/\omega_m$), a filtering action occurs whereby the concentration field responds mainly to the low-frequency velocity fluctuations. This is a situation for which only the very low-frequency part of the concentration spectrum is described by a pseudosteady state approximation. The concentration fluctuations are created by the $v\,(d\bar{C}/dy)$ term and the magnitude is determined by

$$\frac{\partial c'}{\partial t} \sim v\frac{d\bar{C}}{dy}. \tag{45}$$

Molecular diffusion is important only very close to the wall, ($y < \delta_c$). This damping at high frequencies is manifested by Eq. 7 which, from the arguments given above, would be valid only over a very small range of frequencies if $\sigma\omega_c/\omega_m$ is large.

Comparison of linear theory scaling for mobile (liquid) and immobile (solid) surfaces

Fluctuating velocities normal to the surface cause concentration fluctuations through the term $v\,(d\bar{C}/dy)$. For a mobile surface (a clean water interface) the velocity varies linearly with distance from the surface $v = \beta y$. The magnitude of v therefore decreases linearly with a decrease in δ; the concentration gradient, $d\bar{C}/dy$, increases linearly; and the product remains independent of δ. Thus the magnitude of the term producing concentration fluctuations in the concentration boundary layer is independent of Schmidt number. The consequences of this are that the magnitude of the Reynolds transport depends linearly on the magnitude of $d\bar{C}/dy$ and is independent of Schmidt number, that $\bar{K}$ varies with $S^{-1/2}$, and that the magnitude of the concentration fluctuations are independent of Schmidt number.

For an immobile surface (a solid) the velocity varies quadratically with distance from the surface, $v = \beta y^2$. This causes a dramatically different behavior from a mobile interface. The term creating the concentration fluctuations, $v\,(d\bar{C}/dy)$, decreases with decreasing δ, or with increasing Schmidt number. Mass transfer at immobile surfaces at large Schmidt numbers is usually characterized by small $\sigma\omega_c/\omega_m$ since $\bar{K} \sim S^{-0.7}$ (see Eq. 35). Consequently, the magnitude of the high-frequency concentration fluctuations is determined by

$$\frac{\partial c'}{\partial t} \sim v\frac{d\bar{C}}{dy}. \tag{46}$$

The decrease in $v\,(d\bar{C}/dy)$ with increasing Schmidt number has the effect of decreasing the magnitude of the concentration fluctuations at a given frequency and, in particular, to decrease the relative importance of high-frequency velocity fluctuations. The consequence of this is that mass transfer is usually controlled only by low-frequency velocity fluctuations and that the effective frequency decreases with increasing Schmidt number.

Comparison of linear theory scaling with the nonlinear calculations

The calculations support the physical interpretation obtained from the linear equations in a number of ways: The mass transfer coefficient, $\bar{K}$, is found to vary with $S^{-0.5}$. The spectral function of the mass transfer fluctuations, when plotted as $W_k(\omega)/\bar{K}^2$ vs. ω, for fixed hydrodynamic conditions, does not vary with Schmidt number. The average mass transfer coefficient depends on $(\overline{\beta^2})^{1/4}$ for sufficiently high $\sigma\omega_c/\omega_m$.

Comparison with measurements

Studies of oxygen absorption for cocurrent stratified gas-liquid flow in a channel (McCready and Hanratty, 1985) give $\bar{K}\,S^{1/2} \simeq 0.15$. Figure 2 indicates that for this to be the case,

$\overline{\beta^2} \cong 0.009$. As mentioned in the Introduction, a primary motivation for this research is the interpretation of these measurements of the absorption of a slightly soluble gas. The principal unsolved problem is to characterize the velocity fluctuations in the liquid that are controlling mass transfer. McCready and Hanratty (1984b) have identified a number of sources: turbulence in the gas, wave-induced spatial variations in the interfacial shear stress, turbulence generated at the interface, turbulence generated at the solid boundary, and wave mixing. The significance of the above estimate of $\overline{\beta^2}$ is that the relative importance of different mechanisms can be judged in terms of the magnitude of the velocity gradient fluctuations, $\overline{\beta^2}$, that they generate at the interface.

From such considerations McCready and Hanratty (1985) have argued for the importance of wave-induced spatial variations in the interfacial shear stress. This suggests that $\omega_m \cong 0.7$. This is not quite large enough to be in the range where one should expect a large $\sigma\omega_c/\omega_m$ to be completely correct, yet it is in the range for which the calculations presented in Figure 2 were performed.

Consequently, it is expected that $\overline{K}$ should be primarily dependent on $\overline{\beta^2}$ and only secondarily dependent on ω_m. Equation 43 therefore provides an estimate of how the mass transfer rate is related to the velocity field, provided Eq. 29 is a reasonable approximation of the form of the spectrum.

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Notation

c, C = fluctuating and total concentrations relative to that at the interface made dimensionless with $C_B - C_I$
C_B = bulk concentration
C_I = interfacial concentration
$\overline{C}$ = average total concentration
D = molecular diffusivity
k, K = fluctuating and total mass transfer coefficient made dimensionless with u^*
$\overline{K}$ = average dimensionless mass transfer coefficient
n = frequency, made dimensionless with u^* and ν
S = Schmidt number = ν/D
t = time made dimensionless with u^* and ν
u, U = fluctuating and total streamwise velocities made dimensionless with u^*
u^* = interfacial friction velocity
v, V = fluctuating and total normal velocities made dimensionless with u^*
w, W = fluctuating and total transverse velocities made dimensionless with u^*
$W_k(\omega)$ = spectrum of the fluctuations of k
$W_\beta(\omega)$ = spectrum of the fluctuation β
x = coordinate in streamwise direction made dimensionless with u^* and ν
y = coordinate perpendicular to interface made dimensionless with u^* and ν
z = coordinate transverse to flow made dimensionless with u^* and ν

Greek letters

α = time-varying part of streamwise velocity
β = time-varying part of normal velocity gradient
γ = time-varying part of transverse velocity
λ_z = wavelength of spatial scale in transverse direction made dimensionless with u^* and ν
ν = kinematic viscosity of liquid
$\omega = 2\pi n$, circular frequency

Literature cited

Aisa, L., Caussade, B. George, J., and L. Masbernat, "Exchange of Gas in Stratified Gas-Liquid Flows," *Int. J. Heat Mass Transfer,* **24**(6), 1005 (1981).

Brodkey, R. S., K. N. McKelvey, H. C. Hershey, and S. G. Nychas, "Mass Transfer at the Wall as a Result of Coherent Structures in a Turbulently Flowing Liquid," *Int. J. Heat Mass Transfer,* **21**, 593 (1978).

Campbell, J. A., and T. J. Hanratty, "Mechanism of Turbulent Mass Transfer at a Solid Boundary," *AIChE J.,* **29**(2), 221 (1983).

Lau, K. K., "Study of Turbulent Structure Close to a Wall Using Conditional Sampling Techniques," Ph.D. Thesis, Univ. of Illinois, Urbana (1980).

McCready, M. J., and T. J. Hanratty, "Concentration Fluctuations Close to a Sheared Gas-Liquid Interface," *AIChE J.,* **30**(5), 816 (1984a).

———, "A Comparison of Turbulent Mass Transfer at Gas-Liquid and Solid-Liquid Interfaces," *Gas Transfer at Water Surfaces,* W. Brutsaert and G. H. Jirka, eds., D. Reidel Pub., Boston, 283 (1984b).

McCready, M. J. and T. J. Hanratty, "Measurements of Gas Absorption Rates and Wave Properties for Liquid Films Sheared by a Gas Flow," accepted by *AIChE J.* (1985).

Roache, P. J., *Computational Fluid Dynamics,* Hermosa Pub., Albuquerque, NM (1972).

Shaw, D. A., and T. J. Hanratty, "Influence of Schmidt Number on the Fluctuations of Turbulent Mass Transfer to a Wall," *AIChE J.,* **23**, 160 (1977).

Sirkar K. K., and T. J. Hanratty, "Relation of Turbulent Mass Transfer to a Wall at High Schmidt Numbers to the Velocity Field," *J. Fluid Mech,* **44**, pt. 3, 589 (1970).

Vassiliadou, E., "Turbulent Mass Transfer to a Wall at Large Schmidt Numbers," Ph.D. Thesis, Univ. of Illinois, Urbana (1985).

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