

# Mass Transfer between a Turbulent Fluid and a Solid Boundary: Linear Theory

A linear form of the mass balance equation is used to determine how turbulent transport of mass to a solid wall is related to the fluctuating velocity field. It is found that at high Schmidt numbers the Reynolds transport is controlled by fluctuations of much lower frequency than the most energetic velocity fluctuations. The characteristic of the velocity field that emerges as being most important is the small frequency limiting value of the spectral function of the velocity fluctuations normal to the wall. However, the linear theory that is explored does not predict the correct dependency of the average and the mean-squared deviation of the mass transfer coefficient on Schmidt number. A nonlinear analysis must be performed to examine fully the mechanism of turbulent mass transfer to a solid surface.

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## SCOPE

The chief goals of a theory for mass transfer between a turbulently flowing fluid and a solid boundary are to identify measurable properties of the velocity field which are important and to determine how the time averaged and fluctuating concentration fields are related to these properties. For high Schmidt numbers the concentration boundary-layer is so thin that the velocity field can be represented by the first terms in a Taylor series expansion. For a fully developed flow in the  $x$ -direction the three velocity components are then given as

$$U = \bar{U}(y) + \alpha(x, z, t)y \quad (1)$$

$$v = \beta(x, z, t)y^2 \quad (2)$$

$$w = \gamma(x, z, t)y. \quad (3)$$

The mass balance equation relating the concentration field to these velocity parameters is considerably simplified if a linearization approximation is made whereby terms quadratic in fluctuating quantities are ignored.

Sirkar and Hanratty (1970) successfully used these linear equations to explain the fluctuations in the mass transfer rate to a solid boundary, which are found to be of much lower frequency than the most energetic velocity fluctuations. In this paper this linear theory is used to determine the relation between the Reynolds transport,  $\bar{v}c$ , and the velocity field. The analysis presented differs from recent work of Petty (1975) in that the solutions are obtained in the frequency domain rather than the time domain and in that no simplifying assumptions are made in order to evaluate the integral representing the relation of  $\bar{v}c$  to the spectral function for the velocity field.

## CONCLUSIONS AND SIGNIFICANCE

The most important result derived from the linear analysis is that for mass transfer to a solid boundary at high Schmidt numbers the Reynolds transport is controlled by fluctuations of much lower frequency than the most energetic velocity fluctuations. The physical model that emerges is quite different from classical methods for describing turbulent transport. It is found that the molecular diffusion layer close to a solid wall acts as a filter in that only low frequency velocity fluctuations are effective in transporting mass and in causing concentration fluctuations. As the Schmidt number increases smaller and smaller fractions of the energy of the velocity fluctuations are taking part in the mass transfer process. The characteristic of the fluctuating velocity field that is important is the small frequency limiting value of the spectral function of the velocity fluctuations normal to the wall,  $W_\beta(0)$ .

The reason for this filtering action of the concentration boundary-layer is that the amplitude of velocity fluctuations normal to a solid boundary decreases very rapidly with decreasing  $y$ . Consequently the decrease in the thickness of the concentration boundary-layer with increasing Schmidt number requires a velocity fluctuation be of longer duration in order to cause significant concentration fluctuations.

It is noted, however, that the calculated dependency of mass transfer, via  $\bar{K}$  and  $\bar{k}^2/\bar{K}^2$ , on Schmidt number is not in agreement with experiment. Calculations that include nonlinear terms will improve the accuracy of the prediction of  $\bar{K}$  and  $\bar{k}^2$  (Campbell, 1981). However, the physical picture of the mass transfer process close to a solid boundary suggested by linear theory is not changed.

## BACKGROUND

The mass balance equation relating the time varying concentration field  $C(x, y, z, t)$  to  $U$ ,  $v$  and  $w$  is

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = \frac{1}{S} \left( \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial z^2} \right), \quad (4)$$

where  $S$  is the Schmidt number,  $\nu/D$ , and all quantities have been made dimensionless using the friction velocity,  $u^*$ , the kinematic viscosity,  $\nu$ , and the bulk concentration,  $C_B$ . The dimensionless time

averaged concentration is described by the boundary-layer approximation

$$0 = \frac{1}{S} \frac{d^2 \bar{c}}{dy^2} - \frac{d\bar{v}c}{dy}. \quad (5)$$

Here  $c(x, y, z, t)$  is the fluctuating concentration, given as

$$c = C - \bar{C}, \quad (6)$$

and  $\bar{v}c$  is the dimensionless Reynolds transport term, defined as the time average of the product  $vc$ .

Information about the fluctuating velocity field close to a wall is not complete enough to specify  $\alpha$ ,  $\beta$  and  $\gamma$  so simplified versions of Eq. 4 have to be explored. One which has received considerable attention is the linearization assumption whereby terms nonlinear in the fluctuating quantities are ignored. Equation 4 then becomes

$$\frac{\partial c}{\partial t} + \bar{U} \frac{\partial c}{\partial x} + v \frac{\partial \bar{C}}{\partial y} = \frac{1}{S} \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (7)$$

This is to be solved using the boundary conditions that  $c = 0$  at  $y = 0$  and at large  $y$ . By using order of magnitude arguments, such as given by Sirkar and Hanratty (1970) and Petty (1975), Eq. 7 can be further simplified for large  $S$  to

$$\frac{\partial c}{\partial t} + \beta y^2 \frac{d\bar{C}}{dy} = \frac{1}{S} \frac{\partial^2 c}{\partial y^2}. \quad (8)$$

In this paper we explore the use of Eq. 8 to determine  $(\bar{v}c)$  and to define measurable parameters of the velocity field which control mass transfer to a boundary. The neglect of the terms involving concentration variations in the  $x$  and  $z$  directions is justified provided  $c \rightarrow 0$  rapidly with increasing  $y$  so that gradients in the  $y$  direction are large and the average velocity  $\bar{U}$  is small in the region covered by the concentration boundary layer. Support for this assumption will be provided in the section on Numerical Methods.

We use solutions to Eq. 8 previously presented by Sirkar and Hanratty (1970). In this work the normal velocity  $v$  was represented as

$$v = \hat{v}(\omega) e^{i\omega t} y^2. \quad (9)$$

Since Eq. 8 is linear the fluctuating concentration can be represented as

$$c = \hat{c}(\omega, y) e^{i\omega t}, \quad (10)$$

where the complex function  $\hat{c}(\omega, y)$  is defined by the equation,

$$i\omega \hat{c} + \beta y^2 \frac{d\bar{C}}{dy} = \frac{1}{S} \frac{d^2 \hat{c}}{dy^2}, \quad (11)$$

with  $\hat{c} = 0$  at  $y = 0$  and at large  $y$ .

Sirkar and Hanratty (1970) and Shaw and Hanratty (1977b) used measurements of the fluctuating mass transfer coefficient,

$$k = \frac{1}{S} \left( \frac{\partial c}{\partial y} \right)_{y=0}, \quad (12)$$

to test linear theory. They found that at Schmidt numbers of 2,460 to 7,550 the spatial scale in the transverse direction of the fluctuating concentration field is of the same magnitude as the transverse scales of  $\alpha$  and  $\gamma$ . However, the frequency of the mass transfer fluctuations was found to be over an order of magnitude smaller than the frequency of the velocity fluctuations in the immediate vicinity of the wall. Solutions to Eq. 11 for  $\omega \gg 1/S$  provide an interpretation of these results by showing the role of molecular diffusion in damping concentration fluctuations close to a wall and by giving an accurate prediction of the asymptotic behavior of the frequency spectrum for  $k$  at large  $\omega$ . According to this high frequency solution the influence of molecular diffusion is confined to a vanishingly small fraction of the concentration boundary-layer as the Schmidt number approaches infinity.

The first use of a Fourier modes analysis to calculate the concentration fluctuations close to a boundary was made by W. O. Criminals (private communication, also cited by Notter and

Sleicher, 1969). The first attempt to evaluate Reynolds stresses by using solutions to the linear equations was made by Notter and Sleicher (1969), who determined the limiting behavior of  $\bar{v}c$  for  $y \rightarrow 0$ . Shaw and Hanratty (1977b) also used solutions of Eq. 11 to infer the spatial variation of  $\bar{v}c$  and to show that the analogy between momentum and mass transfer is not a valid means of relating  $\bar{v}c$  to properties of the turbulence. As had previously been done by Sleicher and Notter, they showed that  $\bar{v}c$  varies as  $y^3$  for  $y \rightarrow 0$ . However, they also pointed out that this result could be of limited use since it applies only to a small part of the concentration boundary layer for large  $S$ .

The first comprehensive attempt to use linear theory to calculate the variation of  $\bar{v}c$  over the entire concentration boundary layer is contained in a series of papers by Petty (1975, 1978) and Petty and Wood (1980). Their solution is carried out in the time domain, so that it does not show the filtering by the concentration boundary-layer as clearly as do the solutions presented in this paper. The results are given in terms of a Green's function and the velocity field is represented by the autocorrelation of  $\beta$ . Instead of numerically evaluating the resulting integral representation of the solution, further simplifications involving a "smoothing assumption" and a series expansion of the Green's function were made which lead to an analytical equation for the mass transfer coefficient given as

$$\bar{K} \sim S^{-7/10}. \quad (13)$$

This Schmidt number dependency of  $\bar{K}$  is in remarkably close agreement with the experimental results of Shaw and Hanratty (1977a), although the calculated magnitudes of  $\bar{K}$  are 50% larger.

In this paper general solutions of Eq. 11, valid at any frequency, are used to calculate the relation of the frequency spectra of  $c^2$  and of  $\bar{v}c$  to the frequency spectrum of  $\beta$ . It is found, contrary to some of the discussions presented by Shaw and Hanratty, that energetic velocity fluctuations are not controlling the mass transfer process. The solution indicates that, as Schmidt number increases, progressively smaller frequencies and progressively smaller fractions of the total energy of the velocity fluctuations are directly important to the mass transfer process. The magnitude of  $\bar{v}c$  is therefore related to the velocity field through the limiting behavior of the spectral function for  $\beta$  as  $\omega \rightarrow 0$ ,  $W_\beta(0) = \beta^2 \tau_H$ , rather than to the magnitude of the velocity fluctuations, represented by  $\beta^2$ . Differences between Petty's results ( $\bar{v}c \sim \beta^2 \tau_H^{1/2}$ ,  $\bar{K} \sim S^{-7/10}$ ,  $\epsilon/\nu \sim y^{4.5}$ ) and the numerical solution presented in this paper indicate that simplifications used by Petty are introducing significant errors in his calculations.

An actual comparison of calculated values of  $\bar{c}^2$  and of  $\bar{v}c$  with measurements shows that linear theory overestimates these quantities. Furthermore, the calculated magnitude of  $(\bar{k}^2)^{1/2}/\bar{K}$  is much too large to trust results from linear theory. We conclude that a nonlinear form of the mass balance equation needs to be used to do accurate calculations. However, this does not nullify the important result obtained from the linear analysis that the frequency spectrum of  $\beta$  should occupy a central role in attempts to relate the mass transfer rate to the velocity field. This is borne out in calculations carried out by Campbell (1981) for various nonlinear models.

## OUTLINE OF THE ANALYSIS

### Evaluation of the Fourier Transform of $c$

The determination of how the frequency spectrum of  $c(y, t)$  and the cross spectrum of  $v(y, t)$  and  $c(y, t)$  are related to the frequency spectrum of  $\beta(t)$  is facilitated through the use of the Fourier transforms of  $\beta$  and  $c$ , defined as

$$F_\beta(\omega) = \lim_{T \rightarrow \infty} \int_{-T}^T \beta(t) e^{-i\omega t} dt \quad (14)$$

$$F_c(\omega) = \lim_{T \rightarrow \infty} \int_{-T}^T c(t) e^{-i\omega t} dt. \quad (15)$$

The spectral density functions are related to the Fourier transform through the equations

$$W_{\beta}(\omega) = \lim_{T \rightarrow \infty} \frac{F_{\beta}^* F_{\beta}}{T} \quad (16)$$

$$W_c(\omega) = \lim_{T \rightarrow \infty} \frac{F_c^* F_c}{T}, \quad (17)$$

where the \* designates the complex conjugate. The following relations can be written for the autocorrelation functions

$$2\overline{\beta(t)\beta(t-\tau)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} W_{\beta}(\omega) e^{i\omega\tau} d\omega \quad (18)$$

$$2\overline{c(y,t)c(y,t-\tau)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} W_c(\omega) e^{i\omega\tau} d\omega. \quad (19)$$

Since  $W_{\beta}(\omega)$  and  $W_c(\omega)$  are real, symmetric functions the integrals need be evaluated only over the interval 0 to  $\infty$  so that

$$\overline{\beta^2} = \frac{1}{2\pi} \int_0^{\infty} W_{\beta}(\omega) d\omega \quad (20)$$

$$\overline{c^2} = \frac{1}{2\pi} \int_0^{\infty} W_c(\omega) d\omega \quad (21)$$

A relation between  $F_c(\omega, y)$  and  $F_{\beta}(\omega)$  is obtained by taking the Fourier transform of Eq. 8.

$$i\omega F_c + F_{\beta} y^2 \frac{d\overline{C}}{dy} = \frac{1}{S} \frac{d^2 F_c}{dy^2} \quad (22)$$

The full solution to Eq. 22 satisfying the boundary conditions that  $F_c(\omega, 0)$  and  $F_c(\omega, \infty)$  are zero is

$$\tilde{c} = + \frac{1}{2m} \left\{ -e^{-my} \left[ \int_0^y y^2 \frac{d\overline{C}}{dy} e^{my} dy - \int_0^{\infty} y^2 \frac{d\overline{C}}{dy} e^{-my} dy \right] - e^{my} \left[ \int_y^{\infty} y^2 \frac{d\overline{C}}{dy} e^{-my} dy \right] \right\}, \quad (23)$$

where

$$m^2 = i\omega S \quad (24)$$

and

$$F_c = S F_{\beta} \tilde{c}. \quad (25)$$

For small  $y$ , Eq. 23 takes the form

$$\tilde{c} = \frac{2}{m^4} \frac{d\overline{C}}{dy} \left[ \cosh my - \frac{m^2 y^2}{2} - 1 \right] - \frac{\sinh my}{m} \int_0^{\infty} y^2 \frac{d\overline{C}}{dy} e^{-my} dy, \quad (26)$$

where the definite integral is a constant given by

$$\left( \frac{d\tilde{c}}{dy} \right)_{y=0} = - \int_0^{\infty} y^2 \frac{d\overline{C}}{dy} e^{-my} dy \quad (27)$$

#### Evaluation of the Power Spectra of $c$ and $k$

If Eq. 25 is substituted into Eq. 17 the following equation is obtained relating the power spectrum of  $c$  to the power spectrum of  $\beta$ :

$$W_c = S^2 W_{\beta} \tilde{c}^* \tilde{c} \quad (28)$$

From Eqs. 12 and 28 a relation for the power spectrum of the dimensionless fluctuating mass transfer coefficient,  $k$ , can be derived as

$$W_k = W_{\beta} \left( \frac{d\tilde{c}^*}{dy} \frac{d\tilde{c}}{dy} \right)_{y=0}, \quad (29)$$

where  $(d\tilde{c}/dy)_{y=0}$  is evaluated from Eq. 27. For the case of  $\omega S \gg 1$  the term  $d\overline{C}/dy$  in Eq. 27 can be approximated by its value at the wall  $(d\overline{C}/dy)_0 = \overline{K}S$ . The following expression, presented previously by Sirkar and Hanratty and by Shaw and Hanratty (1977) for the limiting behavior of  $W_f$  at large  $\omega$ , is obtained:

$$W_k(\omega) = W_{\beta}(\omega) 4\overline{K}^2 / \omega^3 S \quad (30)$$

For  $\omega = 0$  it is also seen from Eqs. 27 and 29 that

$$W_k(0) = W_{\beta}(0) \left[ \int_0^{\infty} y^2 \frac{d\overline{C}}{dy} dy \right]^2 \quad (31)$$

#### Evaluation of $\overline{vc}$

A spectral function for  $v(y, t) c(y, t - \tau)$  can be evaluated from Eq. 23 using the expression

$$W_{vc}(\omega, y) = \lim_{T \rightarrow \infty} \frac{y^2 F_{\beta}^* F_c(\omega, y)}{T}, \quad (32)$$

since  $F_v = y^2 F_{\beta}$ . From Eq. 32 and 25 the following relation between  $W_{vc}$  and  $W_{\beta}$  is obtained:

$$W_{vc}(\omega, y) = S y^2 W_{\beta}(\omega) \tilde{c}(\omega, y). \quad (33)$$

The cross correlation between  $v$  and  $c$  is expressed in terms of the cross spectrum as follows:

$$2\overline{v(y, t) c(y, t - \tau)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} W_{vc} e^{i\omega\tau} d\omega, \quad (34)$$

where  $W_{vc}$  is a complex function whose real part is even and whose imaginary part is odd. Thus Eq. 34 can be written in the form

$$\overline{v(y, t) c(y, t - \tau)} = \frac{1}{2\pi} \int_0^{\infty} W_{vcR}(\omega) \cos \omega\tau d\omega - \frac{1}{2\pi} \int_0^{\infty} W_{vcI}(\omega) \sin \omega\tau d\omega \quad (35)$$

The Reynolds transport is then obtained by evaluating the above equation for  $\tau \rightarrow 0$ . The use of Eqs. 35, 33 and 23 to calculate  $\overline{vc}$  would give the same results as the one-dimensional Green's function representation of Petty (1975). The chief differences between his results and ours should arise because of approximations he used in evaluating the integral in his Eq. 12.

The use of Eqs. 26 and 32 gives the limiting behavior of

$$W_{vc}(\omega, y) = -y^3 S W_{\beta}(\omega) \int_0^{\infty} y^2 \frac{d\overline{C}}{dy} e^{-my} dy \quad (36)$$

It follows from Eqs. 36 and 35 that  $\overline{vc} \sim y^3$  for  $y \rightarrow 0$ , as derived earlier by Notter and Sleicher (1969) and by Shaw and Hanratty (1977). However, as pointed out earlier, this result is of limited use since it is valid only over a very small portion of the concentration field close to the wall.

#### SCALING OF THE LINEAR SOLUTIONS

A scaling of the linear solutions, valid for all frequencies, can be obtained from an order of magnitude analysis if it is assumed that the thickness of the region where molecular diffusion is affecting the fluctuating concentration field is equal to the thickness of the concentration boundary layer,  $\delta_c$ .

The terms in Eq. 22 are normalized as

$$i\omega \tilde{F}_c + F_{\beta} y^2 \frac{d\tilde{C}}{dy} = \frac{1}{S} \frac{d^2 \tilde{F}_c}{dy^2}, \quad (22)$$

$$\tilde{\omega} \tilde{F}_c \quad F_{\beta} \delta_c^2 \frac{d\tilde{C}}{dy} \quad \frac{1}{S} \frac{\tilde{F}_c}{\delta_c^2}$$

where  $\tilde{\omega}$ ,  $\tilde{F}_c$  represent the magnitudes of  $\tilde{\omega}$  and  $\tilde{F}_c$ . Since all terms in this equation are assumed to be of the same magnitude throughout the concentration boundary layer

$$\tilde{\omega} \tilde{F}_c \sim F_{\beta} \delta_c^2 \frac{\tilde{C}}{\epsilon/\nu} \sim \frac{\tilde{F}_c}{\delta_c^2} \frac{1}{S}. \quad (37)$$

From Eqs. 33 and 34, we find that  $\bar{v}\bar{c}$  scales as  $W_\beta/F_\beta \delta_c^2 \bar{\omega} \bar{F}_c$ . Therefore, it follows from Eq. 37 that

$$\frac{\epsilon}{\nu} \sim W_\beta \delta_c^4 \quad (38)$$

$$\bar{\omega} \sim \frac{1}{\delta_c^2 S} \quad (39)$$

The thickness of the concentration boundary-layer is obtained by considering the integral of Eq. 5,

$$\bar{K} = \left[ \frac{1}{S} \frac{d\bar{C}}{dy} - \frac{\epsilon}{\nu} \frac{d\bar{C}}{dy} \right] \quad (40)$$

It is assumed that  $\delta_c$  is defined as a region where the two terms in brackets are of the same magnitude. It follows that

$$\delta_c \sim W_\beta^{-1/4} S^{-1/4} \quad (41)$$

and

$$\bar{\omega} \sim S^{-1/2} W_\beta^{1/2} \quad (42)$$

From the integral of Eq. 40,

$$1/\bar{K} = \int_0^{\delta_c} \frac{S}{\left(1 + S \frac{\epsilon}{\nu}\right)} dy, \quad (43)$$

we obtain the following scaling for  $\bar{K}$ :

$$\bar{K} \sim S^{-1} \delta_c^{-1} \sim W_\beta^{1/4} S^{-3/4}. \quad (44)$$

The relationships of Eqs. 38, 39, 41, 42, and 44 are consistent with the results presented in Figures 5, 6, 7 and 8 discussed in the next section.

## NUMERICAL METHODS

Equation 23 was solved at different fixed values of  $\omega$  and  $y$  by using a Hamming predictor-corrector numerical integration routine in double precision. These calculated values of  $\bar{c}$  were then substituted into Eqs. 29 and 33 to evaluate  $W_k(\omega)$  and  $W_{vc}(\omega, y)$ . The Reynolds transport term  $\bar{v}\bar{c}$  was obtained from  $W_{vc}(\omega, y)$  by performing the integration of Eq. 35 using Simpson's rule.

The value of  $d\bar{C}/dy$  used in Eq. 23 was determined by an iterative scheme. A function representing  $d\bar{C}/dy(y)$  was assumed. Equation 5 was then integrated using the calculated values of  $\bar{v}\bar{c}$  to determine whether the assumed function was correct. If not, a new representation of  $d\bar{C}/dy$  was assumed and the numerical integration was repeated.

The initial guess of  $d\bar{C}/dy$  was

$$\left(\frac{d\bar{C}}{dy}\right)_1 = (\bar{K})_1 S / \left[1 + S \left(\frac{\epsilon}{\nu}\right)_1\right] \quad (45)$$

where

$$(\bar{K})_1 = 0.089 S^{-0.704} \quad (46)$$

and

$$\left(\frac{\epsilon}{\nu}\right)_1 = 0.0004 y^4 \quad (47)$$

Values of  $-(\bar{v}\bar{c})_1$  determined with this first guess were used to evaluate  $(\epsilon/\nu)_2 = (\bar{v}\bar{c})_1 / (d\bar{C}/dy)_1$ . A second guess  $(d\bar{C}/dy)_2$  was chosen as follows:

$$\left(\frac{d\bar{C}}{dy}\right)_2 = (\bar{K})_2 S / \left[1 + S \left(\frac{\epsilon}{\nu}\right)_2\right] \quad (48)$$

where

$$1/(\bar{K})_2 = \int_0^\infty \frac{S}{1 + S \left(\frac{\epsilon}{\nu}\right)_2} dy \quad (49)$$

By using this method a stable solution was obtained within three iterations.

Different values of  $y_\infty$  and  $\omega_\infty$  were tried to determine a region where the location of the outer boundaries of the integrations did not affect the solution. It was found that  $\bar{K}_{\text{final}}$  and the shape of  $d\bar{C}/dy$  changed less than about 2 per cent for  $y_\infty S^{1/4} > 20$  and  $\omega_\infty S^{1/2} > 0.19$ . The initial conditions were also varied and found not to affect the final solution.

## RESULTS

A comparison of the spectral function of  $W_k(\omega)$ , measured by Shaw (1976), and the spectral function of the transverse component of the velocity gradient at the wall,  $W_\gamma$ , is given in Figure 1. We assume that  $W_\beta$  and  $W_\gamma$  have similar shapes. We note that all of the energy of the mass transfer fluctuations are contained in a region where  $W_\gamma$  is a constant. Therefore, in the calculations we take

$$W_\beta(\omega) = W_\beta(0) \quad (50)$$

A value of  $W_\beta(0) = 0.010$  was determined by fitting the high frequency measurements of  $W_k(\omega)$  to the high frequency solution derived from linear theory.

$$W_k = \frac{4\bar{K}^2}{\omega^3 S} W_\beta \quad (51)$$

The comparison of the calculated  $W_k(\omega)$  with measurements at  $S = 695$  shown in Figure 1 clearly shows that linear theory overestimates  $W_k(\omega)$  at low frequencies. The results of calculations at different  $S$  given in Figure 2 show that a universal curve can be obtained by plotting  $W_k S / W_\beta(0)$  versus  $\omega S^{1/2}$ , as suggested by the scaling discussed earlier.

A typical calculated variation of  $\bar{c}_R$  with  $y$  is given in Figure 3. A comparison is also given with the solution for  $y \rightarrow 0$  used in deriving Eq. 36. Figure 4 gives the calculated spectral function of the Reynolds transport,  $\bar{v}\bar{c}$ , at  $S = 1000$ . A comparison with Figure 1 shows that turbulent transport of mass is not controlled by the most energetic velocity fluctuations. At a larger Schmidt number the dominant frequency of  $W_{vc}(\omega)$  shifts to a lower value. Thus linear theory indicates that smaller and smaller amounts of the energy of the velocity field are effective in controlling mass transfer as the Schmidt number increases.

The calculated variations of  $\bar{v}\bar{c}$ ,  $d\bar{C}/dy$  and  $\epsilon/\nu$  with  $y$  are given in Figures 5, 6 and 7. It is noted that a simple power law does not provide a good representation of the function describing the variation of  $\epsilon/\nu$ . These results are best represented by saying that linear theory gives  $(\epsilon/\nu) S$  as a universal function of  $y S^{1/4}$ .

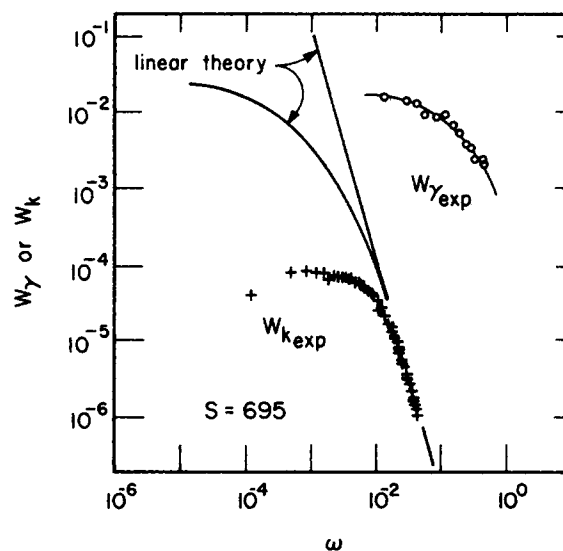


Figure 1. Experimental spectra compared with linear theory results.

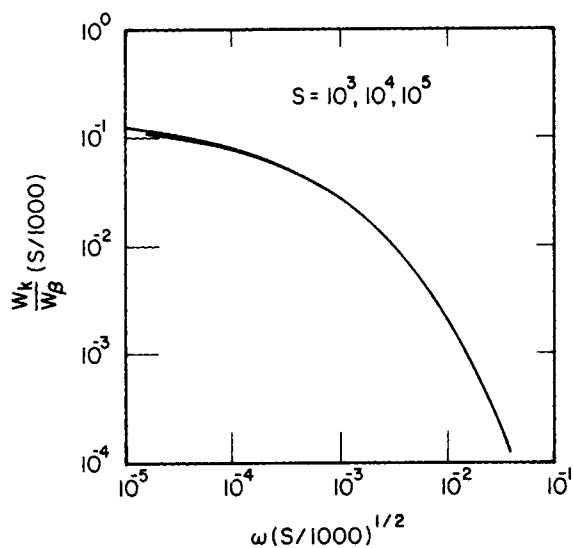


Figure 2. Spectra mass transfer coefficient at various Schmidt numbers from linear theory.

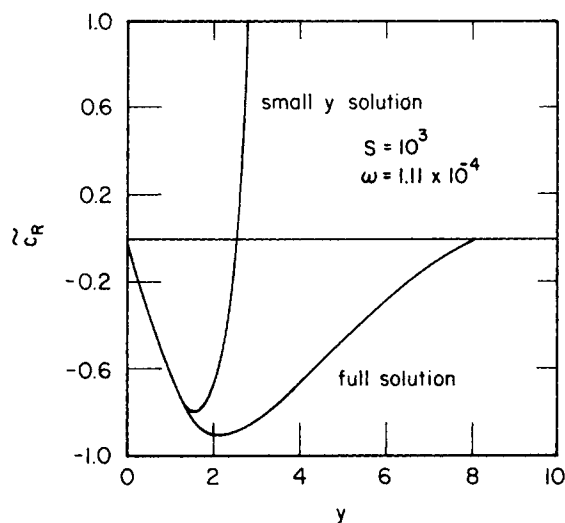


Figure 3. Variation of  $\bar{c}_R$  with  $y$  at a particular frequency from linear theory.

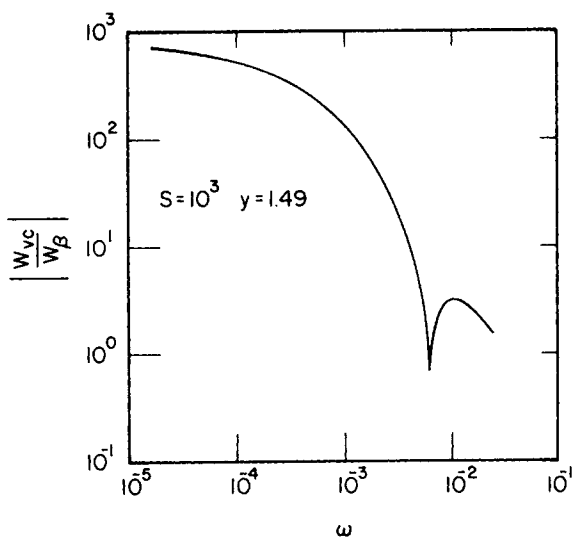


Figure 4. Spectrum of Reynolds transport calculated from linear theory.

Values of  $\bar{K}$  calculated from linear theory are given in Figure 8. These give  $\bar{K} \sim S^{-3/4}$ . A comparison with measurements shows that linear theory predicts values of  $\bar{K}$  which are too high. This is

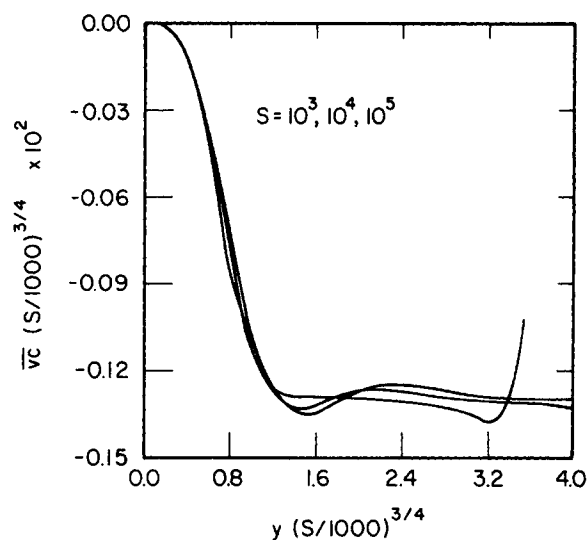


Figure 5. Reynolds transport results from linear theory.

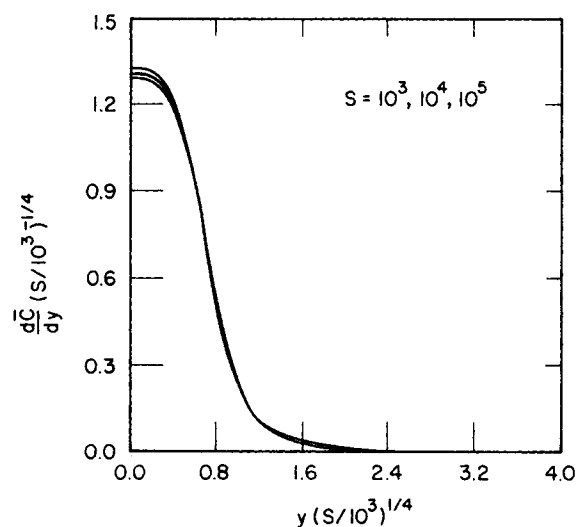


Figure 6. Concentration gradient results from linear theory.

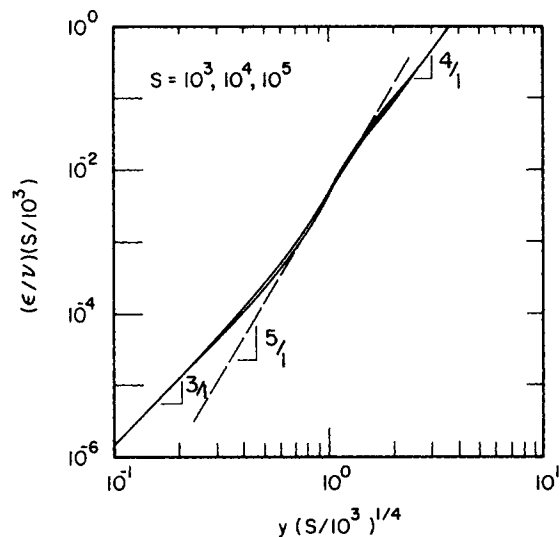


Figure 7. Eddy diffusivity results from linear theory.

consistent with the observation that linear theory predicts values of the fluctuating concentration field which are too high. For example, by using the results shown in Figures 2 and 8, we obtain  $(\bar{k}^2)^{1/2} / \bar{K} = 1.56$ , independent of Schmidt number.

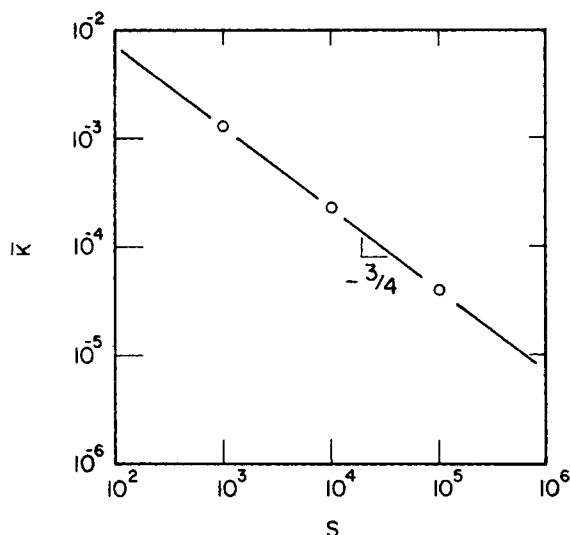


Figure 8. Average mass transfer coefficient from linear theory.

The disagreement of the calculations presented in this paper with measurements could be associated with the use of the simplified Eq. 8 rather than the full linear Eq. 7. However, a more likely explanation is that the poor agreement results from the neglect of nonlinear terms. Support for this interpretation can be obtained from recent numerical solutions of nonlinear mass balance equations by Campbell (1981).

#### INTERPRETATION

A physical interpretation of the filtering action of the concentration boundary-layer displayed by the solution to the linear equations can be obtained from a consideration of the scaling presented in Section 3 and of the recent analysis by McCready (1981).

According to Eq. 8, concentration fluctuations close to a solid boundary are caused by the term  $v \, d\bar{C}/dy = \beta y^2 \, d\bar{C}/dy$ . As the Schmidt number increases, the concentration boundary-layer becomes thinner and the derivative  $d\bar{C}/dy$  increases. However, it is to be noted that since  $v \sim \beta y^2$  the amplitude of the velocity fluctuations decreases much more rapidly than  $d\bar{C}/dy$  increases. In order for a fluctuation in  $v \, d\bar{C}/dy$  to cause an appreciable fluctuation in the concentration,  $c$ , its duration must increase if the Schmidt number increases. Consequently as the Schmidt number increases the effective velocity fluctuations are of lower frequency.

According to this interpretation the filtering becomes less effective if the variation of  $v$  with distance from the boundary is of lower order. This has recently been demonstrated by McCready (1981) for the case of a mobile boundary for which  $v = \beta y$ . This can also be seen if the order of magnitude analysis in Section 3 is repeated for the case in which  $v$  is varying linearly with distance from the wall. It is then found that the characteristic frequency of the concentration fluctuations is independent of Schmidt number, i.e.,  $\tilde{\omega} \sim W_\beta S^0$ .

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#### NOTATION

- $\tilde{c}$  =  $F_c/SF_\beta$
- $c, C$  = fluctuating and total concentrations made dimensionless with bulk concentration,  $C_B$
- $D$  = molecular diffusivity,  $\text{cm}^2/\text{s}$
- $F_\beta$  = Fourier transform of time varying  $\beta$

- $F_c$  = Fourier transform of time varying  $c$
- $F_v$  =  $y^2 F_\beta$
- $k, K$  = fluctuating and total mass transfer coefficient made dimensionless with  $u^*$
- $m$  = factor in linearized equation =  $\sqrt{i\omega S}$
- $S$  = Schmidt number =  $\nu/D$
- $t$  = time made dimensionless with  $u^*$  and  $\nu$
- $T$  = period of time made dimensionless with  $u^*$  and  $\nu$
- $u^*$  = friction velocity,  $\text{cm/s}$
- $u, U$  = fluctuating the total streamwise velocities made dimensionless with  $u^*$
- $v$  = fluctuating normal velocity made dimensionless with  $u^*$
- $W_\beta$  = spectrum of the fluctuation  $\beta$
- $W_\gamma$  = spectrum of the fluctuation  $\gamma$
- $W_c$  = spectrum of the fluctuation  $c$
- $W_k$  = spectrum of the fluctuation  $k$
- $W_{vc}$  = cross spectrum of the product of the fluctuations  $v$  and  $c$
- $w$  = fluctuating transverse velocity made dimensionless with  $u^*$
- $x$  = coordinate in the flow direction made dimensionless with  $u^*$  and  $\nu$
- $y$  = coordinate perpendicular to wall made dimensionless with  $u^*$  and  $\nu$
- $z$  = coordinate in the transverse direction made dimensionless with  $u^*$  and  $\nu$

#### Greek Letters

- $\alpha$  = time varying part of dimensionless streamwise velocity =  $u/y$
- $\beta$  = time varying part of dimensionless normal velocity =  $v/y^2$
- $\gamma$  = time varying part of dimensionless transverse velocity =  $w/y$
- $\delta_c$  = thickness of the concentration boundary layer made dimensionless with  $u^*$  and  $\nu$
- $\epsilon$  = eddy diffusivity,  $\text{cm}^2/\text{s}$
- $\nu$  = kinematic viscosity,  $\text{cm}^2/\text{s}$
- $\tau$  = time delay made dimensionless with  $u^*$  and  $\nu$
- $\tau_H$  = Eulerian time scale of  $\beta$
- $\omega$  = circular frequency made dimensionless with  $u^*$  and  $\nu$

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