BNL-61801

CONF-950853--5

GAS MASS TRANSFER FOR STRATIFIED FLOWS*

R. B. Duffey
Brookhaven National Laboratory
Upton, NY 11973

E. D. Hughes
CSA Inc.,
Idaho Falls, Idaho 83405

ABSTRACT

We analyzed gas absorption and release in water bodies using existing surface renewal theory. We show a new relation between turbulent momentum and mass transfer from gas to water, including the effects of waves and wave roughness, by evaluating the equilibrum integral turbulent dissipation due to energy transfer to the water from the wind. Using Kolmogoroff turbulence arguments the gas transfer velocity, or mass transfer coefficient, is then naturally and straightforwardly obtained as a non-linear function of the wind speed drag coefficient and the square root of the molecular diffusion coefficient.

In dimensionless form, the theory predicts the turbulent Sherwood number to be $Sh_t = (2/\sqrt{\pi})\, Sc^{1/2}$, where Sh_t is based on an integral dissipation length scale in the air. The theory confirms the observed nonlinear variation of the mass transfer coefficient as a function of the wind speed; gives the correct transition with turbulence-centered models for smooth surfaces at low speeds; and predicts experimental data from both laboratory and environmental measurements within the data scatter. The differences between the available laboratory and field data measurements are due to the large differences in the drag coefficient between wind tunnels and oceans. The results also imply that the effect of direct aeration due to bubble entrainment at wave breaking is no more than a 20% increase in the mass transfer for the highest speeds.

The theory has importance to mass transfer in both the geophysical and chemical engineering literature.

*This research was supported by the U. S. Department of Energy under Contract No. DE-AC07-76IDO1570 and Contract No. DE-AC02-76CH00016.

STATEMENT OF THE PROBLEM OF WIND AND GAS FLOW OVER WATER

The turbulent motion of the liquid determines the mass transfer rate in geophysical and chemical engineering processes, when a wind or gas flows over the surface and waves may be present. Gases are absorbed into and released from water at the interface between the water surface and the environment due to the concentration gradient at the surface. We provide a relationship that is generally applicable to many gases, and only depends on the local gas speed.

The basic theory of mass transfer depends on transport across a thin turbulent boundary layer in the liquid that is affected by the presence of the waves (*Jahne et al.*, 1989; *Hanratty*, 1991). Existing methods, models, correlations, and theories for gas mass transfer at the air-water interface all contain assumptions and do not predict the experimental data without adjustment, or are just empiricial fits. There are also significant scatter in the data, and large differences are observed between the laboratory and field data. The books edited by Brutsaert and Jirka (1984), and by Stevens and Gulliver (1991), for example, contain many models and studies of the mass transfer process.

One fundamental model is surface renewal theory in which turbulent eddies in the liquid are characterized by particular scales (*Brtko and Kabel*, 1978). The difficulty has been in the selection of the appropriate length and velocity scales, which have been somewhat objectively adopted as fractions of depths, wavelengths and mean flows. Recently, Musschenga et al. (1992) have demonstrated the applicability of the theory to pipe flow.

In our previous paper (*Hughes and Duffey*, 1991) we extended the application of the surface renewal theory to the case of interface mass and heat transfer in shallow flows or liquid layers where the presence of both the interface and the wall or bottom shear had to be included. We derived the integral dissipation with a mean shear of the interface, verified against data, and illustrated consistency with existing empirical correlations.

To include wave effects, we utilize the existing ideas that the wind over the waves produces turbulence and turbulent dissipation in the liquid. Therefore, we have extended our previous theory of integral dissipation to deep liquids where the turbulence is due to the presence of waves and breakers, (*Chao et al.*, 1976). We use the hypothesis that the integral dissipation in the wind is a measure of the turbulent energy flux that leads to the generation and dissipation of liquid turbulence. This hypothesis is validated by comparison of predictions with data. We show the observed differences in momentum transfer (i.e., the drag coefficient) between laboratory and field data give corresponding differences in mass transfer rate. We use the previously published data on drag coefficients directly and without adjustment to predict the mass transfer, an approach pioneered by *Deacon* (1977) and *Brtko and Kabel* (1978).

Furthermore, we demonstrate consistency with the turbulence-centered theory of Banerjee (1991, 1992) for low speeds on smooth surfaces (without waves), which utilizes the concepts of surface renewal and turbulent bursts.

PREVIOUS WORK AND LITERATURE ON GAS MASS TRANSFER TO WATER BODIES

There is an extensive and complicated literature on mass transfer (see e.g. the review by Hanratty, 1990). As pointed out by Coantic (1986), gas transfer into the oceans is not well understood, and a variety of approaches has been adopted to date to model the interfacial phenomena. As the wind increases, the interface regime changes from a smooth calm surface, to two-dimensional capilliary waves, to large breakers. Thus treating the water as rough or smooth, rigid or moving, and deep or shallow have all entered as variations in the literature. We treat the effect of waves on the mass transfer through the observed variation in turbulent momentum transfer, as developed by Brtko and Kabel (1978) and others.

The gas transfer velocity, or mass transfer coefficient, is dependent on the shear due to the turbulent wind blowing over the rough and wavy water surface, because the momentum transfer generates turbulence in the water to transport the gas-laden liquid from the surface into the bulk liquid below (*Brtko and Kabel,* 1978); *Csanady,* 1985). At moderate to higher wind speeds, the turbulence in the water is dominated by the wind, with turbulence due to the mean motion of the body of water less significant.

Several models for the transfer velocity have been developed based on assumptions for the wind shear, surface roughness, turbulence modelling in the water and air, the effects of the compliant free interface on the turbulence, and sub-surface transport. These models are reviewed in the recent paper by Hanratty (1990). Thus, Deacon's (1977) classic work took a velocity profile over a smooth surface and equated the wind shear to that close to the water surface. With the adoption of a wind-speed dependent drag coefficient, CO_2 transfer rates were estimated to within a factor of two of measured rates, as also shown by Keeling (1965) and Hasse and Liss (1980), but with an dependency on diffusivity to the 2/3 power. Similar factor of two agreement was obtained by Brtko and Kabel (1978) using large and small eddy scales in a surface renewal model, with a standard drag correlation.

Later theories and experiments considered the surface roughness and waves explicitly, arguing that the wave motion, breaking and subsequent intense stirring, contributes in some undefined manner to the turbulent (fluctuating) momentum and mass transport (*Coantic*, 1986; *Jahne et al.*, 1987; *Murata et al.*, 1991). Csanady (1985) developed arguments of shear stress and flow separation over short waves to provide an equilibrium turbulent energy transport from the wind to the water. In fact, Kitaigorodskii and Donelan (1984) suggested using isotropic turbulence simply because of the wave action at the surface. However, they argue against the use of surface renewal in the presence of waves. We agree with these ideas, in the sense that we adopt a Kolmorogoff scale for the equilibrium turbulent dissipation where the energy input to the water and the turbulent dissipation, is in balance with the dissipation caused by gas flow over a rough (wavy) surface. This physical model is consistent with Csanady's (1985) analysis of the transfer process. However, as shown by Chao et al., (1976) we argue that, the presence of waves, and indeed breakers, simply adds to the dissipation in the liquid through the action of the surface drag caused by the wind field. Hence wave effects can be included naturally in the dissipation in the surface renewal theory. We do not consider local turbulent patches in the liquid (see e.g., *Rashidi et al.*, 1991), but rather evaluate the integral turbulent energy flux. The effect of bubble aeration due to entrainment by wave action is considered later.

Mass transfer relations as a function of wind speed have also been described by Liss and Merlivat (1986) with a series of three equations fitted to the regimes of smooth, rough, and breaking surfaces, respectively. These equations fit the available data also to within a factor of two (*Watson et al.*, 1991). The recent measurements by Watson et al., (1991) show a nonlinear dependency of the CO_2 transfer velocity on wind speed (i.e. the surface drag coefficient is not constant). The measured gas transfer velocity data from Watson et al. are in quantitative agreement with the data compilation reported by Hasse and Liss (1980) and the data of Fortescue and Pearson (1967) for lakes and rivers. The latest correlation for lakes by Wanninkhok et al., (1990) also shows a non-linear variation in mass transfer coefficient with wind speed, as do the latest wind tunnel data of Jahne et al., (1989). Since these relations are largely empirical, we were motivated to provide an alternative and consistent physical theory for the mass transfer, where transition between regimes occurs naturally (if at all) and no additional empirical constants are needed to fit the data.

This brings us to the question of the use and applicability of surface renewal theory, which is well accepted in chemical engineering for mass, heat and momentum transfer (*Banerjee*, 1991, *Musshenga et al*, (1992), as noted above. The theory requires an estimate of length and velocity scales, which typically have been unique or adjusted to each application. Thus, Fortescue and Pearson (1967) adopted the Dankwerts surface renewal theory of turbulent eddies and took characteristic velocity and

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

length scales as 10% of the mean velocity and depth, respectively. Agreement with mass transfer data both for rivers and open channel flows was obtained with the renewal period formed with these scales. The results of Dickey et al., (1983) and Ledwell (1984) for turbulent conditions show the gas transfer velocity varies as the square root of the molecular diffusivity, D_m, and inversely with the square root of the observed surface renewal period, t_r, for oxygen, nitrogen, radon, helium, nitrous oxide, methane, and carbon dioxide. This dependency on the square root of the molecular diffusivity and renewal period is in agreement with surface renewal theory and has been validated to agree with a wide range of gas absorption data (e.g., *Jahne et al.*, 1989). Brtko and Kabel (1985) subsequently took a length scaled corresponding to 10% of the wind-mixed layer for large eddies, or a fraction of the Morin-Oburkhow length for eddy cells. The results vaired from the data by factors of 2-3, and they suggested using a transition between the models as functions of turbulent Reynolds number.

Kitaigorodskii and Donelan (1984) propose using the Kolmogoroff turbulence scale because of the presence of wave breaking and foaming, and for gas transfer across air-water interfaces.

However, wave breaking itself is not the controlling mechanism (*Jahne et al.*, 1987), and turbulent transport from the air dominates. Khoo and Sonin (1992) have observed a change in the slope of the k_l curve and noted that in the literature of gas absorption in atmospheric flows, the change in slope is postulated to be associated with wave breaking. However, with their experimental system, the change in slope was not related to wave breaking and bubble entrainment as no waves were present (only ripples of about 1-2 mm in amplitude). We also note that renewal theory successfully predicts heat and mass transfer in turbulent separated flows (*Hughes and Duffey*, 1991) when the surface is rough.

We attempt to unify the geophysical and chemical mass transfer literature, and derive one relation to cover both laboratory and field data.

SURFACE RENEWAL THEORY AND EQUILIBRIUM INTEGRAL DISSIPATION

Surface renewal is caused by turbulent eddies at a roughened surface. The turbulent dissipation variation near the surface, as discussed by Csanady (1985), Coantic (1986) and others, is handled by using the equilibrium balance between the integral dissipation associated with the shear in the wind blowing over the surface and the dissipation into the liquids due to induced turbulent momentum flux in the liquid consistent with these results and observations.

In the usual surface renewal theory in which turbulent eddies in the bulk water are transported to and from the water–air interface, the gas is absorbed by molecular diffusion at the interface which is rough and wavy and sheared by the wind. The mass transfer coefficient is simply

$$k_1 \sim D_m^{1/2}\left(\frac{1}{t_r}\right)^{1/2} \qquad (1)$$

where t_r is the average renewal period which are taken as Kolmorogoff length and velocity scales. To estimate the dissipation, we will need to know the wind drag coefficient over the water (*Brtko and Kabel*, 1978).

Integral Dissipation Theory for Wind Over Rough Water

Consider the wind blowing with speed U_g over a rough water surface with roughness z_0 due to the wind. A representation of the flow field near the gas–water interface is shown in Figure 1 which we have adapted from Fabre et al., (1984). The basic features of the flow and the nomenclature used in this paper are shown in the figure. We assume that:

(1) The average transport is governed by the motion of turbulent eddies on the liquid side as is generally accepted.
(2) The surface and any waves can be treated as a characteristic roughness presented to the wind.
(3) The velocity profiles are fully-developed, turbulent, and in steady state.
(4) The turbulent eddies are wind driven via shear and wave motion.
(5) The wind shear can be represented by a drag coefficient formulation which includes all wave effects.
(6) Bottom shear is neglected.
(7) The effect of aeration by wave breaking on the mass transfer is neglected.
(8) In equilibrium, an energy balance exists between the turbulence generated by the wind and the dissipation in the liquid.

If we were to proceed to attempt to evaluate the turbulence characteristics and dissipation in the liquid, we would need to model the exceedingly complex flow field at a free wavy interface (*Csanady*, (1985), *Street*, 1979). We evaluate the dissipation from the integral dissipation balance of Csanady (1985), thus avoiding detailed modeling of the flow field in the liquid. Continuity of the viscous shear at the air-water interface is assured by the momentum jump condition; thus, the shear in the water near the interface can be accurately taken to be that due to the air.

Now, by solving the equation for molecular diffusion of concentration into the water, the gas transfer velocity (mass transfer coefficient) is simply (*Higbie*, 1935; *Brtko and Kabel*, 1978)

$$k_1 = \frac{2}{\sqrt{\pi}}\left(\frac{D_m}{t_r}\right)^{1/2} \qquad (2)$$

The average surface renewal period, t_r, is related to the turbulent dissipation rate per unit mass, ε, by

$$t_r = \left(\frac{\nu_\ell}{\varepsilon}\right)^{1/2} \qquad (3)$$

where ν_l is the viscosity of water. This derivation follows the suggestion of Kitaigorodskii and Donelan (1984) of using Kolmogoroff length, $\left(\frac{\nu_\ell^3}{\varepsilon}\right)^{1/4}$ and velocity, $\left(\frac{\nu_\ell}{\varepsilon}\right)^{1/4}$, scales to estimate the renewal time. It is well established that in the absence of an interface, surface renewal theory accurately predicts heat, mass, and momentum transfer (*Musschenga et al,* 1992).

The shear due to the wind generates waves and turbulence in the liquid, *(Csanady, 1985)*. We postulate *the turbulent energy flux in the air is in equilibrium with the turbulent dissipation in the liquid through the action of interfacial shear.* Kitaigorodskii and Donelan (1984) argue that this hypothesis can apply only for low Reynolds number in the absence of wave breaking but as can now be seen, we have included these effects via the Kolmorogoff turbulence model. This hypothesis is supported by the observations of Chao et al., (1976), and we test it by the scientific method of comparisons to data.

Thus, although the exact mechanisms of momentum transfer are still debated, we know the wind energy is transmitted to the water by the shear stress with form drag being negligible. In equilibrium, the energy supply from the air to the surface must be dissipated by the eddies in the turbulent liquid. This energy supply has been argued by Csanady (1985) as due to the non-uniform shear stress. There is consequently an enhanced Reynolds stress distribution in the air due to the waves.

The total liquid dissipation can be written as the sum of the mean shear dissipation, ε_m, in the liquid and the turbulent dissipation in the gas due to the waves, ε_t, so

$$< \varepsilon > = \varepsilon_m + \varepsilon_t \; .$$

The mass transfer is now

$$k_\ell = 2\left(\frac{D_m}{\pi}\right)^{1/2}\left(\frac{\varepsilon}{\nu_\ell}\right)^{1/4}$$

To obtain ε_t, the local dissipation in the air above the water, is,

$$\varepsilon(y) = k^2 y^2 \left(\frac{du}{dy}\right)^3 \quad (4)$$

where k is von Karman's constant (k=0.4). For flow over a fully-rough surface the velocity distribution is, Schlichting (1968),

$$u = \frac{u_*}{k} \,\mathrm{Ln}\left(y/z_0\right) + B \quad (5)$$

where B is a constant, u_* is the friction velocity $(\tau_i/\rho_g)^{1/2}$, τ_i is the interfacial shear stress, z_0 is a measure of the surface roughness, and, k the Von Karman constant. From Eq. (5) du/dy $=u_*/ky$ and the local dissipation from Eq. (4) is

$$\varepsilon(y) = \frac{u_*^3}{ky} \quad (6)$$

The average dissipation is obtained by integrating over a height, Z_{10}, above the water surface from the roughness height, z_0, i. e.

$$\varepsilon = \frac{1}{Z_{10}} \int_{Z_0}^{Z_{10}} \varepsilon(y)\,dy \quad (7)$$

or,

$$\varepsilon = \frac{u_*^3}{Z_{10} k} \,\ell n\left(\frac{Z_{10}}{Z_o}\right) \quad (8)$$

Equation (8) shows that the dissipation in the air scales as the cube of the shear velocity. This result we previously obtained (*Hughes and Duffey*, 1991), for liquid film flows applicable to the outer regions of the film near the free surface.

The effective roughness height for the ocean surface in the presence of waves ranges from about $10^{-4} < Z_0 < 1$m (*Hasse and Liss*, 1980; *Wu*, 1969) depending on wind speed. As taken by Coantic (1986) and Deacon (1977) amongst others, the momentum jump condition at the air–water interface requires the shear stress in the liquid to be equal to the shear stress in the air. The friction velocity in the liquid $u_* = (\tau_i/\rho_\ell)^{1/2}$ and $\tau_\ell = \tau_i$, hence

$$u_* = \left(\frac{C_D \rho_g U_{10}^2}{\rho_\ell}\right)^{1/2} \quad (9)$$

where U_{10} is the wind speed at a reference height (usually 10 meters) above the surface (where it is known) and C_D the drag (wind stress) coefficient.

Substituting Eq. (9) into Eq. (8) and that result into Eqs. (3) and(1), we obtain the *constitutive law for the gas transfer velocity over rough surfaces,*

$$k_l = 2\left(\frac{D_m}{\pi}\right)^{1/2}\left(\frac{C_D\rho_g}{\rho_\ell}\right)^{3/8}\left(\frac{1}{kZ_{10}\nu_\ell}\right)^{1/4} \ell n\left(\frac{Z_{10}}{Z_0}\right)^{1/4} U_{10}^{3/4} \quad (10)$$

where with SI units k_l has units m s^{-1}. This is a general formulation for k_l and it is insensitive to the values adopted for the characteristic height above the interface, Z_{10}, and surface roughness, Z_0. The dependence of the mass transfer velocity on wind speed then varies as $C_D^{3/8}\,U_{10}^{3/4}$. This new result highlights the need to accurately know the surface drag coefficient characterizing the momentum transfer, and plainly the mass transfer can only be predicted to that same accuracy.

To obtain ε_m, Banerjee's (1991) result for low speed flow when the surface does not appear fully rough in open channels can be written as,

$$k_l = K\left(\frac{C_D\rho_g}{\rho_\ell}\right)^{1/2}\left(\frac{D_m}{\nu_\ell}\right)^{1/2} U_{10} \qquad (11)$$

where K is 0.158 to 0.108 as derived from comparisons to data.

If we interpret this to be due to the dissipation due to the mean shear over a smooth surface, this corresponds to

$$\varepsilon_m = \left(\frac{K\pi^2}{2}\right)^4 \left(\frac{C_D\rho_g}{\rho\ell}\right)^2 u_4^{10}$$

The transition from motion over a smooth surface to motion over a wavy or roughened surface can now be consistently accounted for in our model.

We expect $k_{Lm} << k_{lt}$, with a value of order 10^{-5} ms-1 (e.g., *Hasse and Liss*, 1980, *Yu, Hamrick, and Lee*, 1984) for velocities < 3 ms^{-1} ; to be weakly dependent of wind speed, as observed; and well represented by Banerjee's result for stratified flows (equation (11)).

The final result is then, from the above discussion,

$$k_l = K\left(\frac{C_D\rho_g}{\rho_\ell}\right)^{1/2}\left(\frac{D_m}{\nu_\ell}\right)^{1/2} U_{10}$$

$$\left[1+\left\{\frac{2}{K\sqrt{\pi}}\right\}\left(\frac{\nu_\ell}{kZ_{10}U_{10}}\right)\ell n\left(\frac{Z_{10}}{Z_0}\right)^{1/4}\left(\frac{\rho_g}{\rho_\ell}C_D\right)^2\right]^{1/2} \qquad (12)$$

This formulation consistently combines the mass transfer for smooth and rough surfaces, including naturally the physics of turbulent bursts, waves, and gas properties.

The result, Eq. (10 and 11) for the mass transfer coefficient, is insensitive to the values chosen for the "characteristic" quantities k, Z_0, and Z_{10} as they appear to the 1/4 power at most. The value of von Karman's k is universally taken as 0.4, without debate. Actually Z_{10} is a given quantity for each case. For oceans, it is usual to take the wind speed U_{10} at 10m above the surface in utilizing the data and hence Z_{10} ~ 10m is a conventional and convenient value for comparison purposes. For wind/water tunnels it is the height of the air space above the water.

In dimensionless form, the mass transfer velocity of Eq. (10) can be written as

$$Sh_t = (2/\sqrt{\pi})\, Sc^{1/2} \qquad (13)$$

where the turbulent Sherwood number is based on the integral dissipation length scale and is

$$Sh_t = k_l\, \eta / D_m \qquad (14)$$

in which the integral dissipation length scale is

and recalling that ε is the integral dissipation given by Eq. (8), and the Schmidt number is (ν/D_m). We note the dependency on the square root of the Schmidt number, and that there is an extremely weak sensitivity to the characteristic roughness, Z_0.The physical meaning of equation (13) is that turbulent mass transport is comparable to molecular diffusion at the interface, a result that is intuitively obvious.

Evaluation of The Drag Coefficient

We find in the geophysical literature that C_D is not in general dimensionless. This is not consistent with the fluid mechanics literature. We think that the formulations in the geophysical literature are indirectly accounting for the effect of wind on the effective roughness of the water surface.

Wu (1969) originally thought that for oceans the wind-stress drag coefficient varies linearly and approaches a constant value C_D~ 2.6 10^{-3} for wind speed greater than about 15 ms^{-1} (at 10 meters above the surface). This erroneous constant value was adopted in textbooks (*Podlosky*, 1987) and values of between 1.1 10^{-3} and 2.6 10^{-3} have been variously reported (*Smethie et al.*, 1985; *Andrie et al.*, 1986). These values are in agreement with values reported for turbulent flow over roughened rigid flat plates (*Schlichting*, 1968) which we interpret and use as an indication that the same general approach should apply as for turbulent boundary layers, as originally proposed by Deacon (1977).

More recently Large and Pond (1981) and Wu (1980) amongst others, has shown that the value is not constant, and a linear variation with speed is more appropriate. For laboratory data, the wind-stress drag varies as the square of the wind speed (Wu, 1969) and is several times greater than the field values. We take the observed drag laws consistent with the data, treat the surface as fully rough as far as the wind is concerned, and demonstrate remarkable insensitivity to the roughness "scale" that is adopted.

In oceanography, the drag coefficient C_D which is taken as a nonlinear function of the form (*Wu*,1980, 1982),

$$C_D = C_{D0}\left(a + bU_{10}^m\right) \qquad (15)$$

where for convenience $C_{D0} \cong 10^{-3}$ and the ranges for a, b, and m are given by Wu. At zero velocity, C_D ~ a C_{D0}, the value for a smooth water surface. Thus from Eqs. (10) and (15), k_l is nonlinear with wind speed. In general, the surface drag coefficient should be a dimensionless function of some characteristics of the surface of the water and the wind speed. Indeed, there is recent work on the effect of wave "age" on the drag (e.g. *Janssen*, 1989; *Nordeng*, 1991; *Toba et al.*, 1990) which requires a known wave spectrum. The formulation of Toba et al., includes parameters describing the wave period, T_s , and the ratio, g, of the wave spectral peak period to a characteristic turbulent period. Their result is

$$C_D = k^2\left[\ell n(2\pi Z_{10}/\gamma) - \ell n\, U_{10} - \ell n\, T_s - 0.5\,\ell n\, C_D\right]^{-2} \qquad (16)$$

For typical ranges of wave period and age, Eq. (16) gives drag coefficients in the same range as Eq. (15) (see Figures 15 through 17 of Toba et al.). In the absence of an accepted general formulation and known values of T_s and γ, Eq. (15) will be used as a guideline for the surface drag coefficient, but we expect that mass transfer will actually also depend on wave age and development.

Many literature studies show that the variation of mass transfer with wind speed can be nonlinear as the surface goes from smooth to wavy to breakers (*Wu*, 1969; *Yu, Hamrick and Lee*, 1984) and the drag also varies with the state of wave development. In addition, laboratory (wind/water tunnel) data exhibit much larger drag coefficients than the field (ocean and lake) data (see *Wu*, 1969), and a stronger (squared) variation with wind speed. We show this increased momentum transfer leads naturally to much larger mass transfer in the laboratory tests.

We examined the C_D correlations of Wu (1969, 1980, 1982), Smith and Banke (1975), Deacon (1977), Wieringa (1974), Geernaert et al., (1986, 1987) as typical of over twenty years of data and reviews for deep and shallow water with a variety of measurement methods. We took the published values for a, b, and m and calculated the C_D values for $1 < U_{10} < 25$ ms^{-1}. We compared these to the widely adopted Wu (1982) values for field data in Equation (15) of a=0.85, b=0.065, and m=1. The mean of all values agreed with Wu's values to within 20%. For laboratory data a much stronger variation with wind speed is observed, and m=2 fits the compilation given by Wu (1969). We adopt these a, b, and m values without stating a preference. It is clear that there is a large and unexplained difference in the field and laboratory data base. We speculate that this is due to different wave development between the relatively shallow flumes and tunnels, and the deeper lakes, rivers and oceans. In fact, it has been shown that non-linear wave growth occurs at fundamentally different rates in shallow and deep liquids (*Duffey* et al., 1978) so that laboratory shear stresses can never agree with field values.

In fact, an effective roughness height, Z_0 , is determined by Eq. (5) and each respective equation for C_D. Rather than calculating an effective roughness height for each formulation for C_D, we take Z_0 as a parameter and cover the ranges that are consistent with the various equations for C_D.

Since the only real variable is the roughness of the surface, Z_0, which is important for its effect on the turbulent velocity in the air above the surface. For moderate wind speed (light winds), with $3 \leq U_{10} \leq 10$ m s^{-1}, Wu (1969) suggests $Z_0 \sim O(10^{-2}m)$; this value was also obtained by Csanady (1985) based on detailed rougheness analysis; and by Hasse and Liss (1980) based on the observed increase of drag coefficient over (smooth) flat-plate values. The theory, Eq. (10) and (11), indicates that roughness variations only appear as a very weak dependency. Somewhat lower values corresponding to a smoother surface have been used by Coantic (1986). We keep to minimum complexity, avoid discussing the dynamics of waves etc., and simply take $Z_0 \sim 10^{-2}$m for all cases.

COMPARISONS TO AVAILABLE WORLD DATA

We next compare our theoretical results with the available data and observations on gas mass transfer in wind tunnels, oceans, rivers, and lakes. Up to this point the theory applies generally to gases being absorbed into liquid bodies. We see immediately the observed dependency on $(D_m)^{1/2}$, and the sensitivity to local pressure as $\rho_g 3/8$. Values for the diffusion coefficient D_m are available in the literature (*Deacon*, 1977; *Broecker and Peng*, 1974 and 1984); and for CO_2 into seawater $D_m \sim 1.6\ 10^{-9}\ m^2\ s^{-1}$, and the Schmidt number, Sc, for CO_2 in seawater is about 600.

We adopt the form given by Eq. (15) noting that the theoretical justification is solely dependent on data comparison. Thus we expect the mass transfer to vary with wind speed as

$$k_l \sim C_{D0}^{3/8}\left(a + b\,U_{10}^{m}\right)^{3/8} U_{10}^{3/4} \qquad (17)$$

which is nonlinear with wind speed as also shown in the data. Since laboratory and field data have m = 2 and m = 1, respectively, we predict a higher mass transfer rate and sensitivity to wind speed in the laboratory. We now proceed to test the theory against existing available data in the same manner as others, but against a wider set.

I. Comparison to Data for Large Stratified Flows: Oceans, Lakes and Rivers

Several data sets are available in the literature and we compare to the most recent compilation as summarized by Watson et al. (1991) for oceans. They included CO_2, radon, and ^{14}C data (the later from atomic weapons tests), and new data from SF_6 and ^3He tracer experiments which were scaled to CO_2. The wind speed ranged over $5 \leq U_{10} \leq 20$ ms^{-1} and include "rough"sea surface conditions. Many of the data points in the figure are a compilation or average of many points and significant additional data exists in the literature at low and moderate wind speeds (*Hasse and Liss*, 1980, *Yu, Hamrick and Lee*, 1984, *Fortescue and Pearson*, 1967, *Jahne et al.*, 1984) which show that the mass transfer coefficient is of the same order. The Watson et al. compilation is only for sea surfaces; however, examination of reaeration data for six rivers and San Diego Bay by Fortescue and Pearson (1967) shows similar values at low speeds. There is considerable scatter on the data, which is why showing an average is convenient as Watson et al., have done.

As an example, comparisons to Eq. (10) are shown in Figure 2 for two values of the zero velocity surface drag coefficient, (2.6 10^{-3} and 1.0 10^{-3}) which bound the range reported in the literature. All calculations are reported for $Z_0 = 0.01$m; calculations with $Z_0 = 0.1$m show little difference from the results reported here. The results in Figure 2 fall somewhat above the data for $C_{D0} = 2.6\ 10^{-3}$, whereas $C_{D0} = 1.0\ 10^{-3}$ provides a good prediction of the data except at the highest wind speed. We observe that the turbulent transport alone explains 100% of the mass transfer for $U_{10} < 15$ ms^{-1}, and 80% above 15 ms^{-1}, using perfectly acceptable and routinely observed drag coefficients.

If an additional mechanism, e.g. direct aeration by bubbles, is needed for the 20% extra above 15 ms^{-1}, this is reasonable but not yet verified. The recent observation of enhanced mass transfer due to wave action (*Wallace and Wirick*, 1992) is not inconsistent with our turbulence model. There is no need to postulate additional aeration mechanisms as waves develop on the surface: the increased drag simply increases the mass transfer. The highest drag value brackets the data, and this increase with C_{D0}=2.6 10^{-3} represents an upper theoretical bound on the mass transfer coefficient. The theory lies close to the global mean ^{14}C data and has a slope $U_{10}^{3/4}$.

The effect of variation in C_D as a function of U_{10} according to Wu's values in Eq. (15) is shown in Figure 3. Also shown in Figure 3 is comparison to the widely-used empirical Liss and Merlivat (1986) relations, while our theory is a continuous line. Substantial agreement with the data in Hasse and Liss (1980) and, as mentioned above, in Fortescue and Pearson (1967) and Yu et al., (1984) is readily verified both in magnitude and the trend with wind speed.

Comparison to the latest data compilation by Wanninkhok et al., (1990) for lakes shows an overprediction of a factor of two at the lowest (< 6 ms^{-1}) speeds (Fig. 4). This is comparable to the variation between data sets evidenced in Fig. 2. for oceans. The Banerjee equation alone (eq. 11) without wave roughness, underpredicts the data. The other line is Wanninkhok et al's empirical fit: we require a reduction in the drag coefficient of a factor of three to fit their data. Why this should be so is not obvious: it suggests further work on drag for lakes would be useful to confirm this effect.

Furthermore we also note that the theory naturally gives a dependency of k_l on Schmidt number, (ν_l/D_m), which varies as $Sc^{1/2}$, a result consistent with the recent values of 0.505 and 0.515 calculated by Watson et al. (1991) on the basis of data obtained with an order of magnitude variation between SF_6 and ^3He.

II. Comparison to Data for Stratified Flow in Wind/Water Tunnels

Several major sets of data are available for a variety of laboratory experiments with wind/water tunnels of varying diameters and shapes, and a wide range of gases and tracers *(Jahne et al.,* 1985; *Jahne et al.,* 1989 ; *Jahne et al.,* 1990). They include CO_2, radon, argon, oxygen, nitrogen oxide, and helium, with wind speeds from $1 < U_{10} < 14$ ms^{-1} and include wavy surfaces. Because of the large range available, we take the latest compilations and results of Jahne et al., (1979, 1985, 1989, 1991) as typical.

In Figure 5, we compare to the results of Jahne et al., (1979) for CO_2 absorption (so called "invasion"), and it can be seen that the increase in absorption with increased waviness is captured. Interestingly, 6 ms^{-1} is exactly the velocity when flooding and flow reversal occurs in thin liquid films (*Duffey et al.,* 1978), which demonstrates the influence of the increased momentum transfer on mass transfer. The mass transfer rates are an order of magnitude larger than the field data (cf Fig. 4). We can see that Banerjee's equation (11) is far too low.

In Figure 6, we compare to the He data of Jahne et al., (1985) and show similar good agreement. To account for the wave effect, we tried equation (15) in equation (11), but it is still too low.

In Figure 7, the theory is compared to the recent data of Jahne et al., (1991) for wind/water tunnels. The theory again accurately predicts the data *using the completely independently derived Wu drag law.*

Thus, we have explained that the large differences in the mass transfer for wind tunnels and large open flows (oceans, lakes and rivers) is due to the observed wind stress difference. We have tested and shown the correct dependencies on gas density, Schmidt number and wind speed. We have shown the increased mass transfer due to the increased drag caused by waves, without recourse to breaking and other enhancing hypotheses.

CONCLUSIONS

The mass transfer rate of wide range of gases (CO2, N_2, O_2, Rn, SF_6, He, Ar and N_2O) at the surface of stratified and wavy water bodies is predictable from turbulent theory. Laboratory wind tunnel data clearly gives much different results from lakes and oceans due to the larger observed shear stress. In particular, the surface renewal theory correctly accounts for the effects of wind speed, roughness due to waves, gas molecular diffusivity, and physical properties. The simple relation derived for the mass transfer coefficient is $Sh_t \sim Sc^{1/2}$, which physically implies a balance between turbulent transport and molecular diffusion. The variation between the theory and data is within the uncertainties of the experimental measurements, and the present state of empirical knowledge of the air drag on wavy surfaces.

The results support the use of renewal theory for mass transfer; and the constitutive law is in substantial agreement with available data. Clearly the dependence on wind speed of the drag coefficient is of major importance in the estimation of gas mass transfer.

REFERENCES

Andrie, C., Oudot, C., Genthon, C. and Merlivat, L. 1986, "CO_2 fluxes in the tropical Atlantic during FOCAL cruises," *J. Geophys. Res.*, **91**, 11714-11755.

Bacastow, R. and Maier-Reimer, E. 1990, "Ocean circulation model of the carbon cycle, "*Climate Dynamics*, **4**, 95-125.

Banerjee, S. 1991, "Turbulence structure and transport mechanisms at interfaces," *Proc. Ninth International Heat Transfer Conf., Paper KN-26,* pp. 395-418, *Hemisphere.*

Banerjee, S. 1992, "Turbulence structures," *Chem. Eng. Sci.*, **47**, No. 8, 1793-1817.

Broecker, W. S., and Peng, T.-H. 1974, "Gas exchange between air and sea,"*Tellus*, **26**, 21–35.

Broecker, W. S., and Peng, T.-H. 1984, "Gas exchange measurements in natural systems, in *Gas Transfer at Water Surfaces,* "edited by W. Brutsaert and G. H. Jirka, pp. 479-493, D. Reidel Publishing Co., Norwell, Mass.

Brtko, W.J. and Kabel, R.L. 1978, "Transfer of gases at natural air-water interfaces," *J. Phys. Oceanography,* **8**, 543-556.

Brutsaert,W. and Jirka, G. H. (editors) 1984, "*Gas Transfer at Water Surfaces,*" D. Reidel Publishing Co., Norwell, Mass.

Chao, S.P., Hsu, E. N., and Street, R. L. 1976, "Wave inducerd velocities and turbulent Reynolds stresses above an air-water interface," Stanford Univ. Tech. Rept. **204**.

Coantic, M. 1986, "A model of gas transfer across air-water interfaces with capillary waves," *J. Geophys. Res.*, **91**, 3925-3943.

Csanady, G.T., 1985, "Air-sea momentum transfer by means of short-crested wavelets," *J. Phys. Oceanography,* **15**, 1486-1501.

Deacon, E. L., 1977, "Gas transfer to and across an air-water interface," *Tellus*, **29**, 363–374.

Dickey, T. D., Hartman, B. and Hurst, E. 1984, "A laboratory technique for investigating the relationship between gas transfer and fluid turbulence, in *Gas Transfer at Water Surfaces*," edited by W. Brutsaert and G. H. Jirka, pp. 93-100, D. Reidel Publishing Co., Norwell, Mass.

Downing, A.L. and Truesdale, G.A. 1955, "Some factors affecting the rate of solution of oxygen in water," *J.Appl. Chem,* **5**, 570- 581.

Duffey, R. B., Ackerman, M. C., Piggott, B. D. G. and Fairbairn, S. A. 1978, "The effects of counter-current single- and two-phase flows on the quenching rate of hot surfaces," *Int. J. Mult. Flow*, **4, 2,** 117-140.

Etcheto, J. and Merlivat, L. 1988, "Satellite determination of the carbon dioxide exchange coefficient at the ocean-atmosphere interface:a first step," *J. Geophys. Res.,* **93**, 15, 669-678.

Fabre, J., Marodon, D., Masbernat, L. and Suzanna, C., 1984, 1984, "Turbulence structure of wavy stratified air-water flow, in *Gas Transfer at Water Surfaces*," edited by W. Brutsaert and G. H. Jirka, pp. 113-123, D. Reidel Publishing Co., Norwell, Mass.

Fortescue, G. E., and Pearson, J. R. A. 1967, "On gas absorption into turbulent liquid," *Chem. Eng. Sci.*, **22**, 1163-1176.

Geernaert, G.L.,Katsaros, K., and Richter, K. 1986, "Variation of the drag coefficient and its dependence on sea state," *J. Geophys. Res.*, **91**, 7667-7679.

Geernaert, G.L., Larsen, S.E. and Hansen, F. 1987, "Measurements of the wind stress, heat flux, and turbulence intensity during storm conditions over the North Sea," *J. Geophys. Res.*, *92*, 13127-13139.

Hanratty, T.J. 1990, "Effect of Gas Flow on Physical Absorption, in *Air-Water Mass Transfer*," ed. S.C. Wilhelms and J.S. Gulliver, pp. 10-33, Am. Soc. Civ. Eng., N.Y.

Hasse, L. and Liss, P. S. 1980, "Gas exchange across the air-sea interface," *Tellus*, **32**, 470–481.

Higbie, R. 1935, "The rate of absorption of a pure gas into a still liquid during short periods of exposure," *AIChE J,* **25**, 122-131.

Hidy, G. M. and Plate,E. J. 1966, "Wind action on water standing in a laboratory channel," *J. Fluid Mech.*, **26**, 651–687,

Hughes, E. D., and Duffey, R. B. 1991, "Direct contact condensation and momentum transfer in turbulent separated flows," *Int. J. Multiphase Flow*, **17**, 599-619.

Jahne, B., Munnich, K.O. and Siegenthaler, U. 1979, "Measurements of gas exchange and momentum transfer in a circular wind tunnel," *Tellus*, **31**, 321-329,

Jahne, B., Wais, T., Memery, L., Caulliez, G., Merlivat, L., Munnich, K. O. and Coantic, M. 1985, "He and Rn gas exchange experiments in the large wind-wave facility," *J. Geophys Res*, **90**, 11989-11997.

Jahne, B., Munnich, K.O., Bosinger, R., Dutzi, A., Huber, W. and Libner, P. 1987, "On the parameters influencing air-water exchange," *J. Geophys. Res.*, **92**, 1937-1949,

Jahne, B., Libner, P., Fischer, R., Billen, T. and Plate, E.J. 1989, "Investigating the transfer processes across the free aqueous viscons boundary layer by the controlled flux method," *Tellus* , **41B**, 177-195.

Jahne, B. 1989, "New experimental results on the parameters influencing air-sea gas exchange," ed. S. Wilhelms and J.S. Gulliver, pp. 582-592, Am. Soc. Civ. Eng., NY.

Janssen, P.A.E.M.1989, "Wave- induced stress and the drag of air flow over sea waves," *J.Phys.Oceonog.*,**19** ,745-754.

Keeling, C. D. 1965, "Carbon dioxide in surface waters of the Pacific Ocean, 2. calculation of the exchange with the atmosphere," *J. Geophys. Res.*, **70**, 6099–6102.

Khoo, Boo-Cheong and Ain A. 1992, "Sonin, Scalar rate correlation at a turbulent liquid free surface: a two-regime correlation for high Schmidt numbers," *Int. J. Heat Mass Trans.*, **35**, 2233-2244.

Kitaigorodskii, S.A. and Donelan, M.A. 1984, "Wind-wave effects on gas transfer," in *Gas Transfer at Water Surfaces*, edited by W. Brutsaert and G. H. Jirka, pp. 147-170, D. Reidel Publishing Co., Norwell, Mass.

Large, W.G. and Pond, S. 1981, "Open Ocean momentum flux measurements in moderate to strong winds," *J. Phys. Oceanography,* **11**, 324-336.

Ledwell, J.J. 1984, "The variation of the gas transfer coefficient with molecular diffusivity," in *Gas Transfer at Water Surfaces*, edited by W. Brutsaert and G. H. Jirka, pp. 293-302, D. Reidel Publishing Co., Norwell, Mass.

Liss, P. S. and Merlivat, L. 1986, "Air-sea gas exchange rates:introduction and synthesis, in *The Role of Air-sea Exchange in Geochemical Cycling, Adv. Sci. Inst. Ser.*," edited by P. Buat-Menard, D. Reidel Publishing Co., Norwell, Mass.

Mearns, L. O., Scneider, S. H., Thompson, S. L. and L. R. McDaniel, 1990, "Analysis of climate variability in general circulation models: comparison with observation and changes in variability in $2XCO_2$ experiments," *J. Geophys. Res.*, **95**, 469-490.

Murata. A, Hihara, E. and T. Saito, 1991, "Turbulence below an air-water interface in a horizontal channel, in *Turbulence Modification in Multiphase Flows*," ASME FED–110, 67-74.

Nordeng,T.E. 1991, "On the wave age dependent drag coefficient and roughness length of the sea," *J. Geophys. Res,96,*7167-7174.

Pearman, G. L., Hyson, P. and Fraser, P. J. 1983, "The global distribution of atmospheric carbon dioxide 1. Aspects of observation and modelling," *J. Geophys. Res.*, **88**, 3581-3590.

Podlovsky, J., 1987, "*Geophysical Fluid Dynamics*," Springer-Verlag, New York.

Rashidi, M., Hetsroni, G., and Banerjee, S. 1991, "Mechanisms of heat and mass transport at gas-liquid interfaces," *Int. J. Heat Mass Transfer*, **34**, 1799-1810.

Schlichting, H., 1968, "Boundary Layer Theory, Chapter xx," pg 581, McGraw-Hill Book Co., New York.

Siegenthaler, S. 1983, "Uptake of excess CO_2 by outcrop diffusion model of the ocean," *J. Geophys. Res.*, **88**, 3599-3608.

Smethie, Jr.,W. M., Takahashi, T., Chipman, D. W. and Ledwell, J. R. 1985, "Gas exchange and CO_2 flux in the tropical Atlantic Ocean determined from ^{222}Rn and $p\,CO_2$ measurements," *J. Geophys. Res.*, 90, 7005-7022.

Smith, S .D. and Banke, E .G. . 1975, "Variation of the sea surface drag coefficient with windspeed," *Quart. J. R. Meteorol. Soc.*, **101**, 665-673.

Street, R.L. 1979, "Turbulent heat and mass transfer across a rough, air-water interface: a simple theory," *Int. J. Heat Mass Transfer*, **22**, 885-899.

Toba,Y., Iida, N., Kawamura, H., Ebuchi, N. and Jones, I. S. F. 1990, "Wave dependence of sea-surface wind stress," *J. Phys. Oceanogr.*, **20**, 705-721.

Wallace, D.W.R. and C.D. Wirick, 1992, "Large air-sea gas flunes associated with breaking waves," *Nature*, 356, 694-696.

Wanninkhof, R., J. Ledwell and Orusius, J. 1990, "Gas transfer velocities on lakes measured with sulfur hexafluoride, in *Air-Water Mass Transfer,"* ed. S. C.Wilhelms and J.S. Gulliver, pp 441-458, Am. Soc. Civ. Eng., NY.

Watson, A. J., Upstill-Goddard, R. C. and Liss, P. S. 1991, "Air-sea gas exchange in rough and stormy seas measured by duel-tracer technique," *Nature*, **349**, 145-147,

Wieringa, J., 1974, "Comparison of three methods for determining strong wind stress over Lake Flevo," *Boundary Layer Meteorol.*, **7**, 3-20.

Wilhelms, S.C. and Gulliver, J.S., (Editors) 1990, "*Air-Water Mass Transfer*," Am. Soc. Civil Eng., NY,

Wu, J. 1969, "Wind stress and surface roughness at air-sea interface," *J. Geophys. Res.*, **74**, 444-455.

Wu, J. 1980, "Wind-stress coefficients over sea surface near neutral conditions - A revisit," *J. Phys. Oceanography*, **10**, 727-740,

Wu, J. 1982, "Wind-stress coefficients over sea surface from breeze to hurricane," *J. Geophys. Res.*, **87**, 9704-9706.

Yu, S. L., Hamrick, J. M. and Lee, D.-S. 1984, "Wind effects on air-water oxygen transfer in a lake, in *Gas Transfer at Water Surfaces*," edited by W. Brutsaert and Jirka, G. H., pp. 357-367, D. Reidel Publishing Co., Norwell, MA.

NOMENCLATURE

a = Constant in drag law
A_i = Water surface area
b = Constant in drag law
C = Gas concentration in the air
C_D = Drag coefficient
D_m = Molecular diffusivity in liquid
k = von Karman constant
k_l = Mass transfer coefficient
K = low speed "constant"
s = Solubility of gas in liquid
Sc = Schmidt number
Sh = Sherwood number
t_r = Renewal period
u = Local speed above liquid
U_g = Wind speed
U_{10} = Wind speed at reference height above surface
y = Distance into liquid
Z_{10} = Characteristic height
Z_0 = Surface roughness
ε = Dissipation per unit mass in the liquid
η = Dissipationlength scale
ν_ℓ = Viscosity of liquid
ρ_g = Gas density
ρ_ℓ = Liquid density
τ = Shear stress

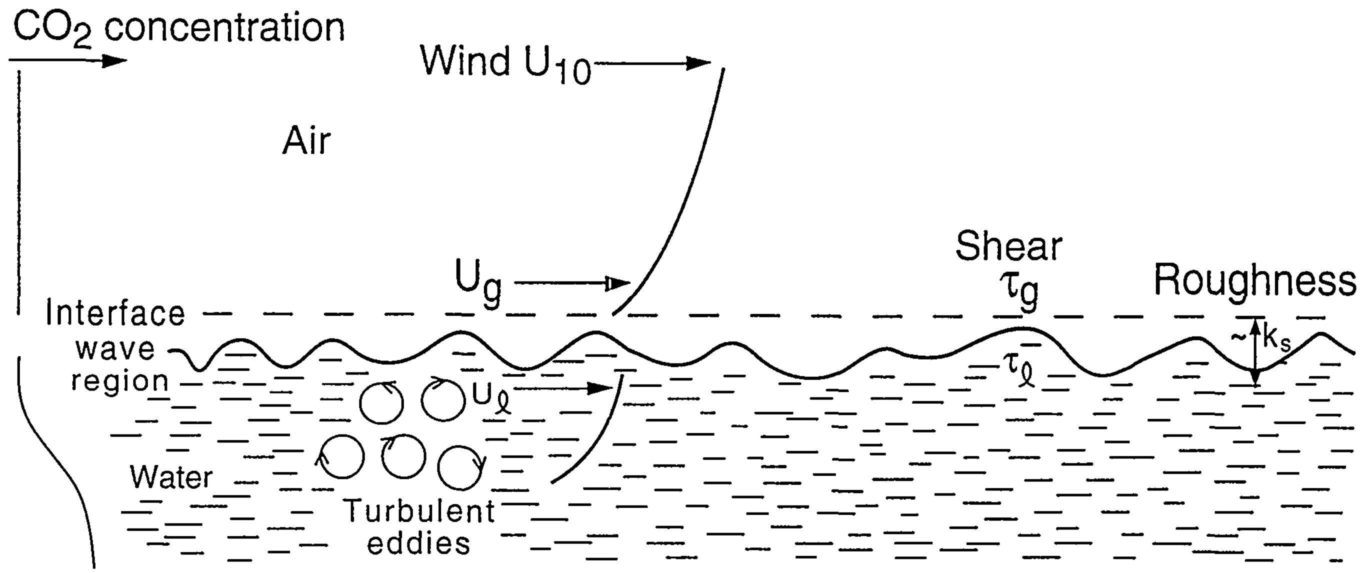

FIGURE 1. SCHEMATIC OF THE FLOW FIELD: WIND OVER STRATIFIED WATER (MODIFIED AFTER *FABRE ET AL*, (1984).

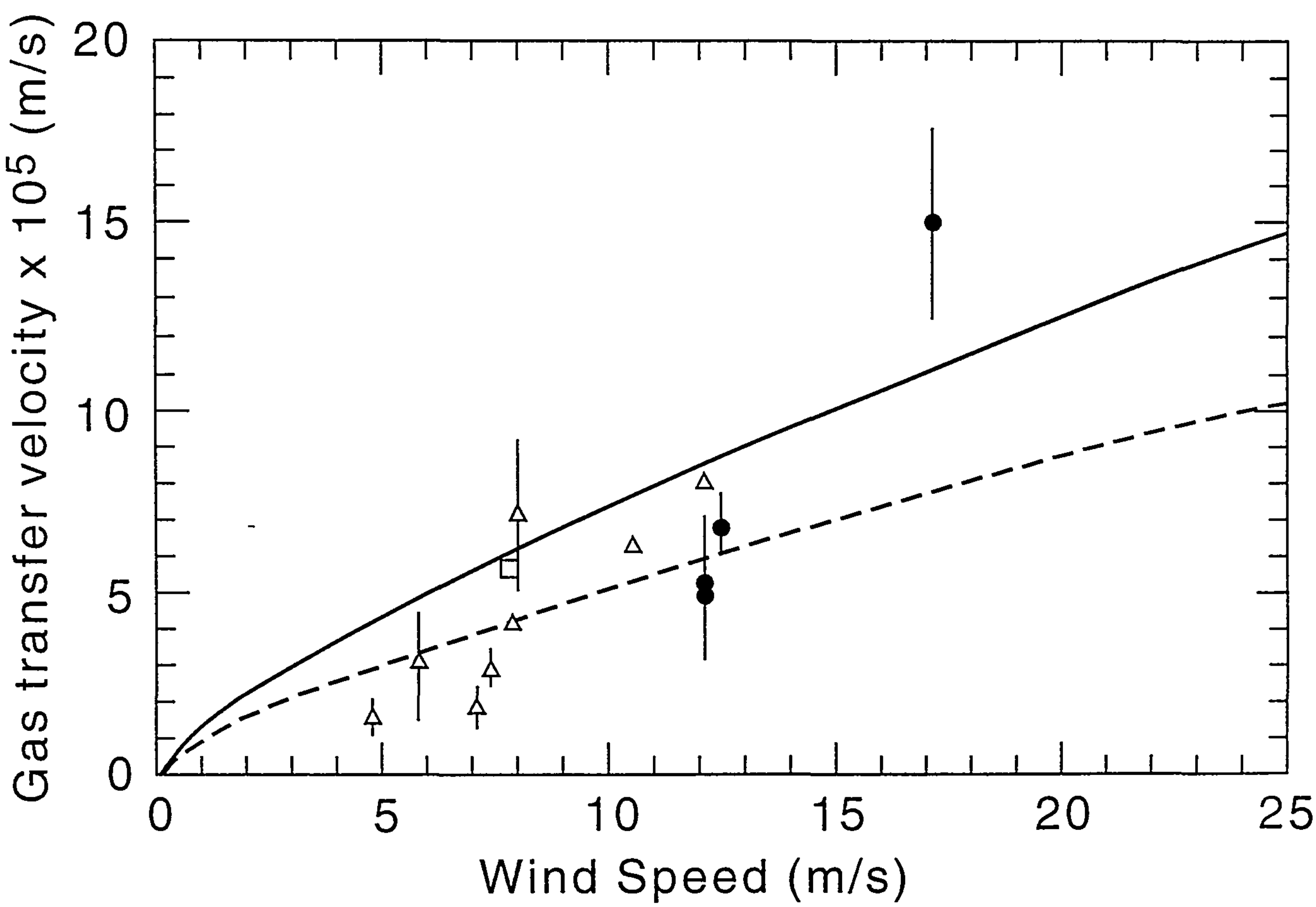

FIGURE 2. COMPARISON OF THEORETICAL PREDICTIONS USING CONSTANT SURFACE DRAG COEFFICIENT TO DATA OF *WATSON ET AL* [1991].

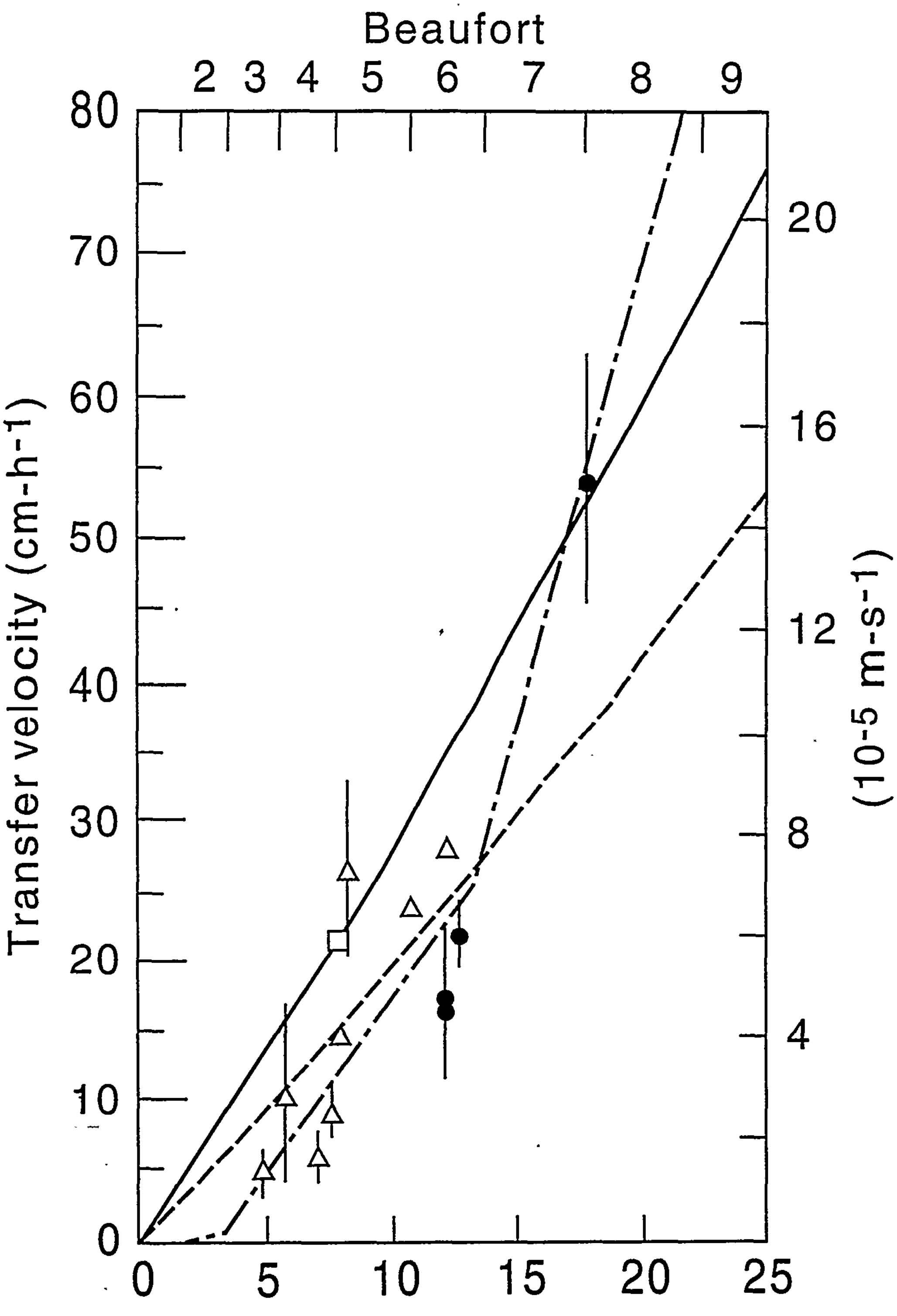

FIGURE 3. COMPARISON OF THEORETICAL PREDICTIONS USING SURFACE DRAG OF EQ. (12) TO DATA OF *WATSON ET AL* [1991] WITH A=0.10 B=0, 10, M=1.0.

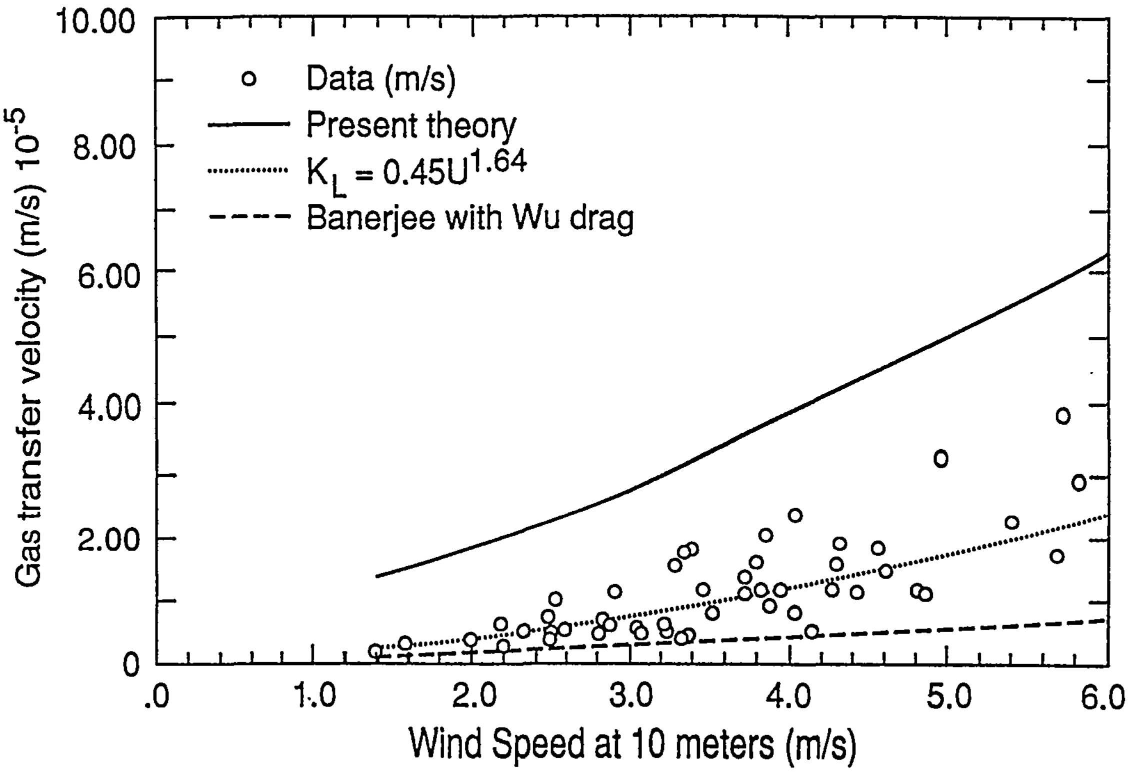

FIGURE 4. COMPARISON OF PREDICTIONS WITH DATA COMPILATION FOR LAKES BY *WANNINKHOK ET AL.* (1990)

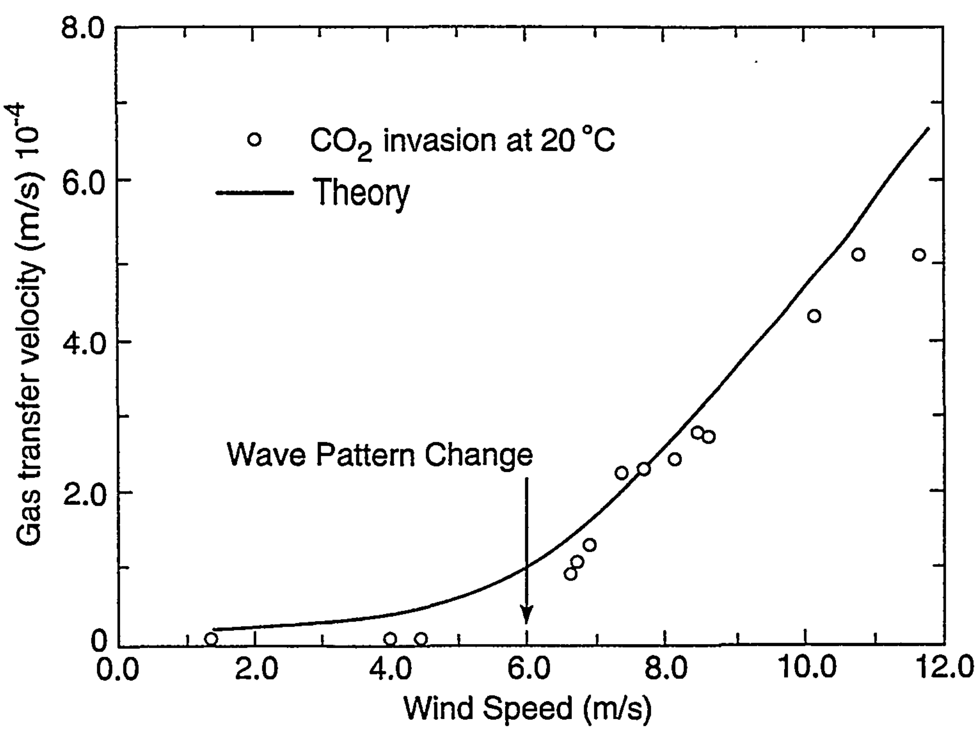

FIGURE 5. COMPARISON OF PREDICTIONS WITH JAHNE DATA (1979) FOR CO_2 INVASION AT HIGH WIND SPEED FROM A CIRCULAR WIND/WATER TUNNEL.

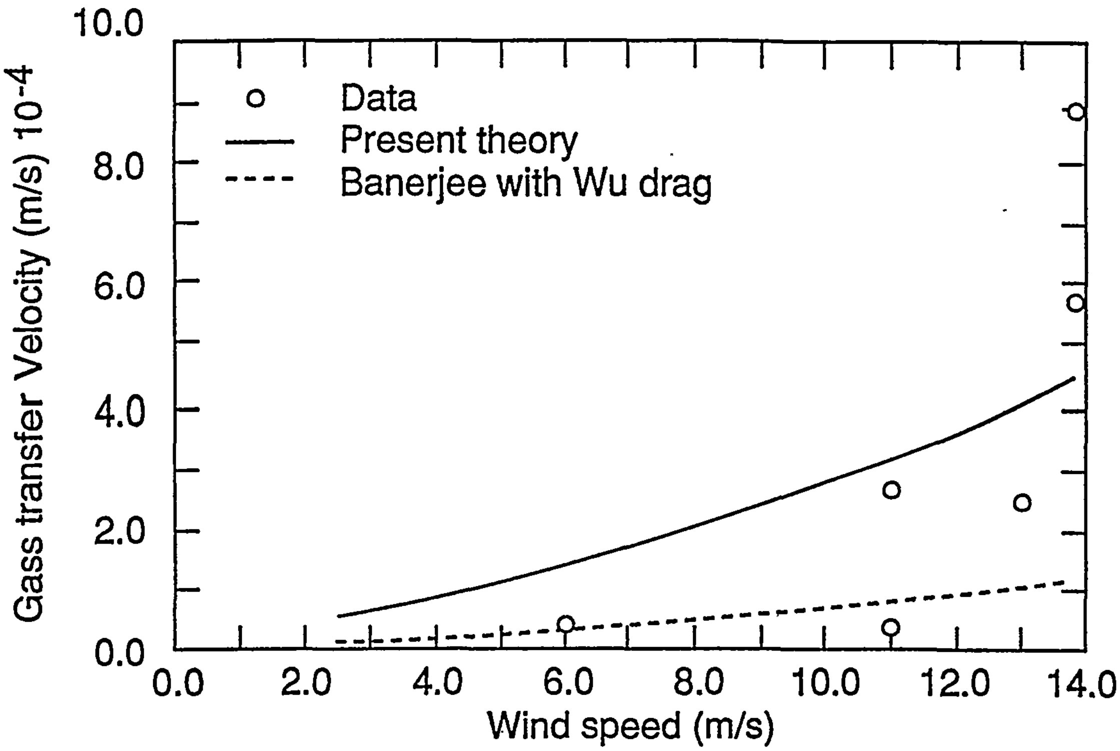

FIGURE 6. COMPARISON OF PREDICTIONS WITH JAHNE (1985) HELIUM DATA UNDER EVASION AND INVASION CONDITIONS FROM A LINEAR WIND/WATER TUNNEL.

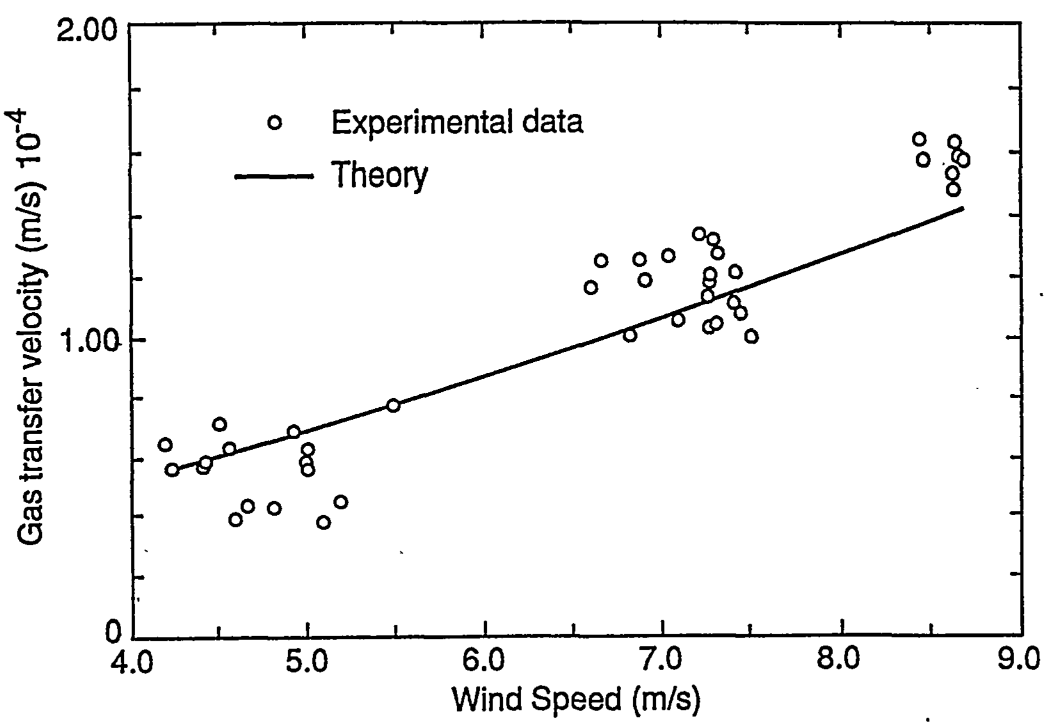

FIGURE 7. COMPARISONS OF PREDICTIONS WITH JAHNE DATA (1991) FOR SC=600 IN WIND/WATER TUNNEL.