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Gas transfer to and across an air–water interface

By E. L. DEACON, *4 Haldane Street, Beaumaris, 3193, Australia*

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ABSTRACT

A treatment based on Reichardt's formulation of the velocity profile in turbulent flow over a smooth plane surface is shown to give good agreement with published data on the boundary layer transfer of heat and mass over a wide range of Prandtl (or Schmidt) number, σ. Applied to transfer to a water surface, agreement with published laboratory results is also good for low air speeds (smooth water). Comparison with observations for the sea shows there is little difference between the calculated evaporation coefficient and those reported for the sea with winds of ~ 7 m s^{-1}. This is consistent with sea trials having so far detected little increase of evaporation and heat transfer coefficients with wind speed over the range 4–10 m s^{-1}.

The air/water transfer of non-reactive gas is governed by the resistance of the viscous sub-layer of water, and the smooth surface treatment gives the transfer velocity (V_L) on a liquid phase basis as

$$V_L = 0.082\,(\rho_a/\rho_w)^{1/2}\sigma^{-2/3}u_*$$

where ρ_a/ρ_w is the density ratio, air/water, and u_* = friction velocity of the surface air flow. The agreement between this formula and published wind tunnel results is good for the smooth water condition. At higher wind speeds transfer exceeds the calculated value and appears then to increase roughly in proportion to the square of the wind speed.

1. Introduction

This paper is directed primarily to improving understanding of transfer between air and sea with the ultimate objective of enabling the estimation of fluxes from air/sea differences. The results may, however, have wider application.

The condition of light winds and smooth or nearly smooth sea is most amenable to treatment in the light of existing knowledge of transfer to rigid smooth surfaces. Crucial to an adequate treatment of heat and mass transfer to smooth plane surfaces from a steady flow of fluid over them is a suitable model of transfer through the viscous sub-layer adjacent to the surface. The experimental difficulty of investigating the detailed structure of these thin layers has led to many formulations based on various hypotheses (see for example Launder & Spalding, 1972). In the following it is shown that a simple treatment based on Reichardt's (1951) formulation of the velocity profile gives satisfactory agreement with published experimental data on heat and mass transfer both to rigid smooth surfaces and to smooth water.

It has been shown by Bolin (1960) that when non-reactive gas is transferring across the interface to bulk liquid, by far the major resistance to transfer is that offered by the viscous sub-layer of liquid on the surface. This is owing to the very much lower molecular diffusion coefficient of gas in the liquid phase than the gaseous. In the case of water the difference amounts to a factor of around 10^4. The same simple treatment applied to the surface skin layer of liquid is compared with data on the rate of transfer of gases to water surfaces secured by Liss (1973) and by Hoover & Berkshire (1969) in wind tunnel experiments. At low air speeds with smooth water the agreement is good, but, as is to be expected, ripples and waves cause a divergence at higher speeds.

Treatments of transfer to surfaces roughened uniformly with closely spaced roughness elements

have been offered by Owen & Thomson (1963) and Yaglom & Kader (1974) among others. These treatments are for the condition of fully rough flow, i.e. roughness large enough for the notion of the existence of a viscous sub-layer in the ordinary sense to be untenable. The flow over water is, in all probability, transitional between smooth and fully rough flow over a wide range of wind speed. This being so then, as stated by Yaglom & Kader (1974), the dimensionless resistance to transfer between surface and observational level will be a function of two Reynolds numbers (the usual smooth surface one and another formed with the average height of the roughness elements), the Schmidt (or Prandtl) number and a number of dimensionless parameters characterizing the shapes of roughness elements, their distribution and also the scatter of their shapes and sizes. It follows that the problem presented by flow over the sea surface is one of formidable complexity as the character of the roughness changes markedly with wind speed. Furthermore the surface is in motion with the various components of the wave spectrum travelling at different speeds. In this context it is difficult to see physical significance for the sea in a Reynolds number constructed with the usual roughness parameter, z_0, from wind profiles as the length component.

It is in view of these complexities that the present contribution is confined to regarding the smooth surface formulations as base relationships useful in studying and comparing the results of wind tunnel and full-scale experiments.

2. Transfer to smooth plane surfaces

In order to apply the Reichardt (1951) velocity profile to the prediction of mass (or heat) transfer in the flow over smooth plane surfaces, it is necessary to make an assumption as to the value of the turbulent Schmidt (or Prandtl) number (α), i.e. the ratio of the turbulent transfer coefficient for momentum to that for the diffusing entity. Reported values of α for the viscous sub-layer are particularly scattered owing to the experimental difficulty of precision measurements so close to the surface. Initially therefore $\alpha = 1$ is assumed, but the fact that this leads to generally satisfactory agreement between observed and calculated rates of transfer (as shown below) may result from some compensation of errors.

Reichardt's velocity profile (see Hinze, 1959, p. 472 and Fig. 7-3) with $\alpha = 1$ gives

$$K_s(z)/D = 1 + k\sigma\zeta_l\{\zeta/\zeta_l - \tanh(\zeta/\zeta_l)\} \qquad (1)$$

in which K_s is the transfer coefficient for the entity for which the molecular diffusion coefficient is D; $\sigma = \nu/D$, ν = kinematic viscosity, k = von Kármán's constant, $\zeta = u_* z/\nu$ and ζ_l = constant. When $\zeta/\zeta_l \gg 1$ then $K_s \to ku_* z$, the familiar result for the logarithmic range of the velocity profile. In this model there is no layer of purely molecular transfer as considered in some earlier formulations and this harmonizes with the fact that some turbulent fluctuation is detectable as close to the surface as it is practicable to measure.

The value of the constant ζ_l has to be chosen so that eq. (1) on integration yields, for the logarithmic region of the velocity profile, the relationship

$$u(z)/u_* = k^{-1} \ln \zeta + B \qquad (2)$$

The values $k = 0.41$ and $B = 5.6$ given by Townsend (1976) correspond to $\zeta_l = 11.7$, a value close to Reichardt's original value of 11.0.

For the layer 0 to $z_v = 50\nu/u_*$ (i.e. to a little above the nominal top of the viscous sub-layers) we have:

$$\text{Resistance to transfer} = \int_0^{z_v} \frac{dz}{K_s}$$

and the dimensionless resistance r_v is given by:

$$r_v = u_* \int_0^{z_v} \frac{dz}{K_s} = \sigma \int_0^{50} \frac{d\zeta}{K_s/D} = \sigma\phi(\sigma) \qquad (3)$$

The function $\phi(\sigma)$ has been evaluated by numerical methods and is shown in Fig. 1. Approximations valid to within 1% are:

$$r_v = 15.2\,\sigma^{0.61} : 0.6 < \sigma < 10 \qquad (4a)$$

$$r_v = 12.1\,\sigma^{2/3} + 2.7 \log_{10}\sigma + 2.90 : \sigma > 10 \qquad (4b)$$

Should α be retained in the treatment and assumed not to vary with z in the viscous sub-layer then $\phi(\sigma/\alpha)$ replaces $\phi(\sigma)$, so that the values of r_v need multiplication by $\alpha^{0.39}$ using eq. (4a) and nearly enough by $\alpha^{1/3}$ in eq. (4b). So even with $\alpha = 0.7$ as suggested by some researches the values of r_v will only be some 10% smaller than given above.

The dimensionless resistance of the layer z_v to z_m (the measurement level for gas concentration, etc.) in the logarithmic regime is $\alpha k^{-1} \ln(z_m/z_v)$ so that

adding resistances gives

$$\frac{\text{Flux}}{\psi_s - \psi_m} = V_m = \frac{u_*}{r_v + \alpha k^{-1} \ln(\zeta_m/50)} \quad (5)$$

where ψ_s, ψ_m are concentrations of gas at the surface and at the measurement level and V_m is the transfer velocity for reference level m. According to Kader & Yaglom (1972) the more reliable laboratory data indicate that $a \approx 0.85$ for the logarithmic layers and this is near to the 0.885 of Chen (1973). In the following $a = 0.85$ is assumed for the logarithmic region.

Eq. (5) may be compared with an expression first given, according to Kader and Yaglom, by Landau and Lifshitz in 1944. This is

$$V_m = \frac{u_*}{\beta(\sigma) + \alpha k^{-1} \ln \zeta} \quad (6)$$

in which $\beta(\sigma)$ is an undetermined universal function of σ. It follows from eqs. (3) and (6) that

$$\phi(\sigma) = \{\beta(\sigma) + \alpha k^{-1} \ln 50\}/\sigma \quad (7)$$

Values of β from many different laboratory investigations are given by Kader & Yaglom (1972) in their Table 1. Taking their mean value of $a/k = 2.12$, the corresponding values of $\phi(\sigma)$ are plotted in Fig. 1. The theoretical curve corresponding to the K_s profile of Eq. (1) fits the experimental data nearly as well as the relationship fitted by Kader and Yaglom. The percentage differences between the two formulae are nowhere more than 6%. An advantage of eq. (5) over eq. (6) is that it makes clear the contribution of the viscous sub-layer to the total resistance to transfer.

The upper inset diagram in Fig. 1 gives the variation of relative resistance, D/K_s, with ζ which shows clearly that at $\sigma = 1000$ the form of the pro-

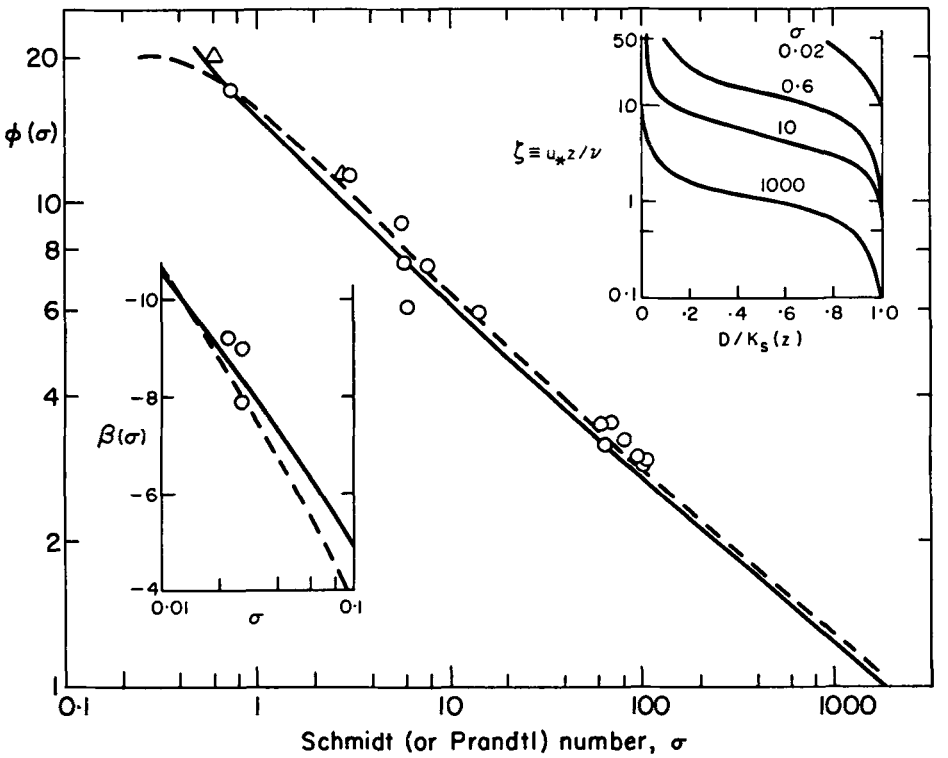

Fig. 1. The function $\phi(\sigma)$ in comparison with observations. The full line is that computed from eqs. (1) and (3), while the broken line is the relationship fitted by Kader & Yaglom (1972) to the experimental values (circles) from laboratory experiments on heat transfer. The point at $\sigma = 0.7$ (air) is from 11 different researches; mean = 17.1 ± 0.18. The triangle points are from Chamberlain's (1968) experiments on water vapour and thorium B vapour transfer from air to a smooth surface. In the lower inset diagram the computed values of $\beta(\sigma)$ of eq. (6) (full line) are compared with Kader and Yaglom's relationship (broken line) and the experimental values for mercury (heat transfer). The upper inset graphs relate relative resistance to transfer, $D/K_s(z)$, to ζ for various Schmidt numbers, σ.

Table 1. *Evaporation from a water surface: comparison of observed transfer velocities (Liss, 1973) with calculation from eq. (5)*

Wind speed*, m s^{-1}	1.6	2.3	3.3	4.2	5.0	6.0	8.2
u_* (Liss), cm s^{-1}	5.8†	12.1†	17.3†	19.0	33.5	31.1	47.3
u_* adopted, cm s^{-1}	8.4	11.7	16.3	21.3	30.7‡	31.9	45.3
V_{10} observed, cm s^{-1}	0.54	0.77	0.93	1.33	1.53	2.07	2.54
V_{10} calculated, cm s^{-1}	0.53	0.71	0.95	1.17	1.62	1.67	2.29
Ratio obsd./calc.	1.02	1.08	0.97	1.13	0.95‡	1.23	1.10

* At 10 cm above water surface.

† Calculated from smooth surface empirical relation eq. (14). For higher speeds u_* adopted is mean of u_* (Liss) for lee end of water surface and $\bar{u}_*$ (smooth) for first metre of fetch.

‡ $u_* = 26$ cm s^{-1} is indicated by fair curve closely fitting u_* *v.* u_{10} plot at all other speeds. This would give obsd./calc. = 1.12.

file below $\zeta = 2$ is very important. For this region eq. (1) on approximation gives the turbulent contribution to K_s equal to $(\frac{1}{3}k\zeta_L^{-2})\nu\zeta^3 = 9.98 \times 10^{-4}\,\nu\zeta^3$. This fully conforms with the deduction of Kader and Yaglom from other experimental results that this contribution is $\approx 0.001\,\nu\zeta^3$.

When $\sigma < 0.6$ eq. (1) indicates that molecular diffusion needs to be taken into account beyond $\zeta = 50$. The experimental results for heat transfer through mercury ($\sigma \approx 0.02$) therefore provide a good test for the validity of eq. (1) when ζ is large. Accordingly $\phi(\sigma)$ of eq. (3) had been computed taking the upper limit of the viscous sub-layers to be where $D/K_s(z) = 0.1$. The corresponding values of $\beta(\sigma)$, which to a close approximation are given by

$$\beta(\sigma) = 8.70\sigma^{2/3} + 4.30 \log \sigma - 2.40;\ 0.01 < \sigma < 0.06.$$

are shown in the lower inset diagram of Fig. 1 in comparison with Kader and Yaglom's empirical relationship and the experimental values given in their Table 1. The simple expression, eq. (1), is seen to have a surprisingly high degree of validity over a great range.

3. Observations of transfer to water surfaces compared with eq. (5).

Laboratory experiments

The transfer of water vapour from a 4.5 m length of water surface in a wind tunnel has been investigated by Liss (1973). These experiments extended to low enough wind speeds (< 3.5 m s^{-1} at $z =$ 10 cm) for the surface to be unruffled (Francis, 1951). Liss gives u_* values estimated from wind profiles near the lee end but these may be somewhat inaccurate, particularly at the lower speeds, owing to the limited fetch. For this reason u_* for the low speeds is estimated from empirical relationships for smooth surfaces, as detailed in the Appendix. At wind speeds above 4 m s^{-1} the profile u_* values are used in eq. (5) after making a correction to allow for the fact that u_* near the lee end of the water surface is not the average for the whole surface needed in the evaporation calculation. The u_* adopted is the mean of that given by Liss and that for the first metre of fetch assumed smooth. The resulting comparison of calculated and observed transfer velocities given in Table 1 shows good agreement for the smooth water condition. Above 4 m s^{-1} there is evidence of some increase in transfer rate above that calculated but only by 20% or so at 6 to 8 m s^{-1}. At these speeds the waves at the lee end of the water surface would average some 1–2 cm in height to judge from Francis (1951).

Möller & Schumann (1970) studied the transfer from air to an area near the lee end of a water surface (total length 3 m) in wind tunnel experiments with a number of vapours and aerosol suspensions covering the range of σ from 0.6 to over 10^5. They isolated the test area by means of plastic strips just high enough to prevent transfer of water but flexible enough not to interfere with the wave motion. With the exception of water vapour, conditions were such that $\psi_s = 0$. They measured transfer velocities at a constant air speed of 8.3 m s^{-1} at 8 cm above the water surface; at this speed they estimated $u_* = 40$ cm s^{-1} from the wind profile. This is anomalously low, as discussed in the Appendix, and $u_* \approx 53$ cm s^{-1} would be expected from the works of Francis (1951) and Liss (1973).

Table 2. *Calculated rates of transfer of water vapour, ThB and various aerosols to a water surface in comparison with the observations of Möller & Schumann (1970)*

Substance		H_2O	ThB	Various aerosols				
Schmidt No. σ		0.60	2.77	3300	3700	4900	5700	8500
Observed V_3, cm s^{-1}		3.70	1.95	0.034	0.030	0.025	0.021	0.016
Observed	A	1.25	1.25	1.75	1.65	1.65	1.5	1.5
Calculated	B	1.2	1.0	1.15	1.1	1.1	1.0	1.0

A: Calculation with $u_* = 53$ cm s^{-1} in eq. (5).
B: Calculation with $u_* = 53$ cm s^{-1} and h = 0.6 cm in eq. (8) from Yaglom and Kader's (1974) rough surface treatment.

Using this value in eq. (5) leads to the comparison given in Table 2. The calculated values are less than those observed as might be expected at this wind speed. Furthermore the variation with σ is somewhat less for the observed values than calculated from eq. (5). This is to be expected with a rough surface according to the treatment of Yaglom & Kader (1974). For rigid rough surfaces they derive

$$V_m/u_* = \{a_1 S_h^{1/2}(\sigma^{2/3} - a_2) + a_3 + ak^{-1} \ln(z_m/h)\}^{-1} \quad (8)$$

in which a_1, a_2, a_3 depend on the shapes and distribution of the roughness elements of mean height h. Mainly from the experimental results of Chamberlain (1968), Yaglom and Kader find that the values $a_1 = 0.55$, $a_2 = 0.2$ and $a_3 = 9.5$, together with $a/k = 2.12$, result in reasonably good agreement for a variety of surfaces, including two with stationary wave-form roughness having a wave height to length ratio of 1 : 10. Table 2 includes a comparison of Möller and Schumann's results with calculation from eq. (8). Agreement within the limits of experimental error is secured taking $h = 0.6$ cm. The mean height of the water waves was about 1 cm to judge from Francis (1951). The motion of the waves could account for the effective height being < 1 cm. The waves in such experiments are relatively simple in form. With the extensive spectrum of waves normal to the sea surface it is hardly to be expected that this kind of treatment can be successfully adapted to air/sea transfer.

Observations of evaporation at sea

During the 1969 BOMEX sea trials near Barbados, Pond et al. (1971) measured the vertical fluxes of momentum, heat and moisture by the eddy correlation technique. To make a comparison between the evaporation rates so observed and calculation from eq. (5), the 7 runs at wind speeds between 6 and 7.5 m s^{-1} (at the 8 m level) were averaged to give:

Mean wind speed = 6.8 m s^{-1}; mean $u_* = 25.6$ cm s^{-1}
Mean Obukhov stability length (L) = −55m
Mean evaporation coefficient, $d_8 = V_8/u_8 = 0.00128$

As the atmospheric conditions were unstable the reduced resistance of the air layers between the top of the viscous sub-layer and the measurement level, 8 m, is allowed for using the following expression for K_H, the eddy conductivity:

$$K_H = k_H u_* z(1 - mz/L)^{1/2} \quad (9)$$

This is applicable to unstable conditions with $k = 0.41$ and $m = 16$ according to Dyer & Hicks (1970) or $k_H = 0.47$, $m = 9$ after Businger et al. (1971). The former values lead to $d_8 = 0.00132$, the latter to $d_8 = 0.00141$. The fact that the observed value, which is nearly the same as that observed under similar conditions by Dunckel et al. (1973), is a little less than calculated from the smooth surface formula, instead of larger as would be expected, is not significant, as Pond et al. consider their evaporation (and drag) coefficients to have an uncertainty of about 20%. That a pronounced increase above the smooth surface value is ruled out is consistent with the results of various sea trials. These indicate the rate of increase of evaporation and heat transfer coefficients with wind speed to be too small to have been reliably assessed as yet.

4. Gas transfer across a plane liquid interface

When a soluble non-reactive gas is being transferred from the air flow to the bulk water (or other liquid) the only considerable resistance is that of the top mm or so of water (Bolin, 1960): this stems from σ being of the order of 10^3 for most gases diffusing in water. The shear stress in this layer will be the same as in the air so the friction velocity (u_*^w) is given in terms of the densities by

$$u_*^w = u_*(\rho_a/\rho_w)^{1/2} \tag{10}$$

For gas transfer the concentration difference actually measured is that between the air and the equilibrium value of the bulk water. To formulate in these terms, the assumption is made that phase equilibrium exists at the interface, an assumption verified experimentally (Scriven & Pigford, 1958). With an unruffled surface the non-dimensional resistance of the viscous sub-layer of water should be as given by eq. (4), and assuming all other resistances to be negligible, one obtains

$$V_G = \frac{Su_*}{(\rho_w/\rho_a)^{1/2} r_v} \approx \frac{0.082 Su_*}{(\rho_w/\rho_a)^{1/2}\sigma^{2/3}} \; ; \; 200 < \sigma < 5000 \tag{11}$$

where S is the solubility of the gas expressed by the concentration ratio liquid/gas. The transfer velocity relative to the liquid phase (V_L) omits S from eq. (11).

For application to air/sea transfer it is convenient to rewrite eq. (11) in terms of the diffusivity (D_{20} cm^2 s^{-1}) of the particular gas in sea water at 20 °C. When account is taken of the variations of air density and sea-water viscosity with temperature and also the Stokes–Einstein relation which gives $\mu D/T$ constant for a given gas diffusing in a solute of viscosity μ, eq. (11) becomes, for the temperature range 0 to 30 °C:

$$V_G \approx 1.21 S D_{20}^{2/3} \; (T/100)^{10} \; (p/1012)^{1/2} \; u_* \times 10^{-6} \tag{12}$$

where T = temperature, K, and p = atmospheric pressure, mb. The fresh water numerical constant is 1.31.

Observational results on gas transfer are frequently reported in terms of the equivalent thickness of laminar film, where

$$\delta_L = D/V_L \tag{13}$$

Comparison with laboratory data

Liss (1973) has measured the rate of transfer of oxygen to water in wind tunnel experiments with a 4.5 m length of water surface. For the calculation of transfer velocities via eq. (11), the u_* values adopted are those of Table 1, as the oxygen and water vapour transfers were observed simultaneously. The resulting comparison is given in Table 3 and Fig. 2.

Hoover & Berkshire (1969) measured the rate of transfer of carbon dioxide to water in wind tunnel experiments with a water surface 2.3 m long. A number of their experiments were made with the water sufficiently acidified (pH $\approx$ 3) for CO_2 to behave as a non-reactive gas. Wind drag on the water was not measured but can be estimated as follows. At wind speeds below 3.2 m s^{-1} the water surface is smooth and u_* may be estimated from the well-established empirical formula for the skin-friction of a smooth rigid surface. Eq. (21.16) of Schlichting (1968) gives

$$\bar{u}_*/u_F = 0.477 \; \{\log_{10} R_l\}^{-1.29} \tag{14}$$

where $\bar{u}_*$ corresponds to the coefficient of total skin friction appropriate to the case where the measured transfer takes place over the whole length l of the

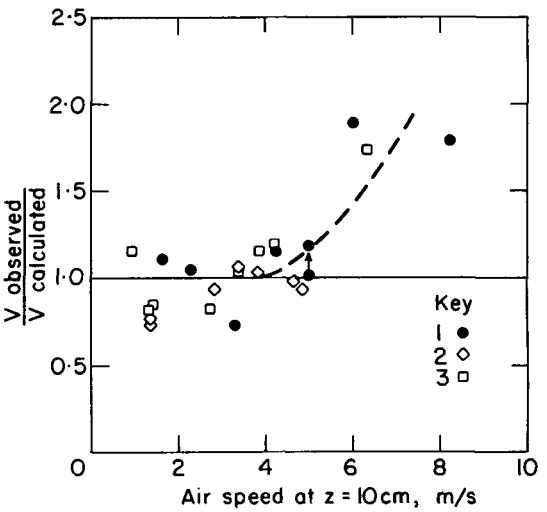

Fig. 2. Wind tunnel results for the transfer of gases to a water surface compared with transfer velocities calculated from eq. (11). 1 Liss (1973)—Oxygen to salt water; 2 Hoover & Berkshire (1969)—CO_2/water pH 3, 20 °C; 3 Hoover & Berkshire (1969)—CO_2/water pH 3, 25 °C. The higher (arrowed) position of the point for O_2 at 5 m s^{-1} is for u_* faired into consistency with those for other speeds (see footnotes to Tables 1 and 2).

Table 3. *Observed rates of transfer of oxygen to salt water (35‰) (Liss, 1973) compared with the rates calculated from eq. (11)*

Wind speed, m s^{-1}		1.6	2.3	3.3	4.2	5.0	6.0	8.2
u_*, cm s^{-1}		8.4	11.7	16.3	21.3	30.7‡	31.9	45.3
Water temperature, °C		11.9	13.5	22.0	13.8	19.3	15.4	17.5
Schmidt No. σ*		850	777	490	762	562	700	620
$V_L(O_2)$ cm s^{-1} × 10^4	obsd.	2.89	4.03	5.33	8.22	12.7	21.4	31.0
	calc.	2.60	3.85	7.27	7.10	12.5	11.3	17.3
Ratio obsd./calc.		1.11	1.05	0.73	1.16	1.02	1.89	1.79

* $D_{20} = 1.93 \times 10^{-5}$ cm^2 s^{-1} (i.e. 4% less than for pure water).

‡ See footnote to Table 1. With $u_* = 26$ cm^{-1} obsd./calc. ratio becomes 1.20 (arrowed point in Fig. 2).

water surface. u_F is the free stream velocity and $R_l = u_F l/\nu$.

For the higher wind speeds u_* may be estimated from the wind tunnel drag measurements of Francis (1951) who used the surface slope technique. His results for the upwind half of his water surface provide a good basis for estimation as the length of water surface (3 m) is comparable. For the requisite range these give

$$u_*/u_{10} \approx 0.0038 u_{10} + 0.033$$

and in applying this the free stream speeds of Hoover and Berkshire were reduced by 10% to make them comparable with those of Francis measured at 10 cm above the water surface. There is good agreement between the two sets of data as may be seen from Fig. 2. The 12 observations with smooth water ($u_{10} < 3.5$ m s^{-1}) give a mean ratio:

Observed/calculated transfer velocity = 0.92 ± 0.05

so there is no significant departure from theory. Above 3.5 m s^{-1} the ratio starts increasing and reaches 2 at ~7 m s^{-1}.

Observations at sea

The only measurements of gas exchange at sea are those of Broecker & Peng (1974) who have developed a method for radon by which the rates of transfer can be calculated from a series of observations of the profile of radon in the water to a depth of some 100 to 200 m. One series of observations is for the trade wind area off Barbados (15° N, 56° W) taken during the BOMEX trials; the other is for the North Pacific (50° N, 145° W) in winter. They give their results in terms of average effective thickness of laminar film, δ_L, which may be compared with the values calculated from eqs. (12) and (13) with D_{20} for radon = 1.14×10^{-5} cm^2 s^{-1}. The resulting comparison is

	Wind speed (m s^{-1})	u^* (cm s^{-1})	T (°C)	δ_L μm obsd.	δ_L μm calc	Ratio calc./obs.
BOMEX	7	26	25	64	140	2.2
N. Pacific	12	56	5	20	77	3.8

For the BOMEX calculation $u_*/u_{10} = 0.037$ is the average value observed by Pond et al. (1971) from eddy correlation runs at wind speeds of ~7 m s^{-1} during the same trials. A 25% higher value is assumed for the North Pacific. The uncertainty in the radon flux measurements is not stated as it is difficult to estimate. It is undoubtedly greater for the North Pacific trials than at BOMEX owing to the much more variable conditions at the former site. However, the indication from these experiments is that ripples and waves considerably increase the rate of gas transfer above that estimated from eq. (12).

5. Carbon dioxide transfer

The transfer of carbon dioxide to the sea is of particular interest in relation to the fate of the vast input to the atmosphere from the burning of fossil

fuels. However, with carbon dioxide there is the complication that it reacts chemically with water at the average pH ≈ 8 of the sea. Chemical reaction increases the transfer velocity to an extent depending on the speed of reaction relative to the time taken for gas molecules to traverse the viscous sublayer. In the case of carbon dioxide an initial analysis by Bolin (1960) suggested that the hydration reaction is slow enough not to affect the rate of transfer between sea and air. More recent treatment by Hoover & Berkshire (1969) and by Quinn & Otto (1971) lead to similar conclusions except that, under light wind conditions, the viscous sublayer can be thick enough for the reaction to have an effect.

Wind tunnel experiments on the rate of transfer of carbon dioxide to water of pH ≈ 6.5, in comparison with the rates for non-reactive gases, have been conducted by Hoover & Berkshire (1969) and by Liss (1973). The two studies agree in finding a pronounced enhancement of transfer rate by the hydration reaction at low air speeds decreasing to zero at about 5 m s^{-1}. The enhancement is about 50% at the 10 cm air speed of 2 m s^{-1} for which u_* $\approx$ 11 cm s^{-1}. At this speed the effective thickness of laminar film given by eqs. (11) and (13) for $\sigma = 550$ and $\nu = 0.010$, is $\delta_L \approx 370$ m. This is within the range of film thickness, 300 to 400 μm, calculated by Quinn & Otto (1971) to correspond to 50% enhancement at pH ≈ 8 on the basis of the stagnant skin-layer model.

For carbon dioxide diffusing in sea-water $D_{20} = 1.62 \times 10^{-5}$ cm s^{-1} and this with $S_{20} = 0.815$ (Li & Tsui, 1971) in eq. (12) gives

$$V_G = 2.95 \times 10^{-5} (p/1012)^{1/2} u_* \text{ (at 20 °C)} \qquad (15)$$

As S varies nearly as $T^{-7.5}$ over the range 5–30 °C, it follows that the coefficient in eq. (15) varies approximately as $T^{2.5}$, i.e. it increases nearly 1% per deg. C. With concentrations expressed in the usual way as parts per million (ppm) by volume eq. (15) leads to:

$$\text{Flux of } CO_2 = 0.048 (p/1012)^{3/2} (1 + 0.007t)(N_s - N_a) u_* \text{ pg cm}^{-2} \text{ s}^{-1} \qquad (16)$$

where N_s is the equilibrium ppm of the surface water and N_a the ppm of the air; p = atmospheric pressure, mb; t = air temperature, deg. C; u_* = friction velocity, cm s^{-1}, and pg = 10^{-12} g.

The laboratory and seagoing observations suggest that eq. (16) should enable transfer rates for carbon dioxide to be estimated within a factor of about 2 at wind speeds up to ~ 10 m s^{-1}. For reasonably steady near-neutral conditions u_* is given by the following formula for the drag coefficient C_D in terms of the wind speed (m s^{-1}) at 10 m above the surface:

$$C_D(10 \text{ m}) = (u_*/u_{10})^2 = (0.95 + 0.05\ u_{10}) \times 10^{-3} \qquad (17)$$

This is based on collation of various sets of eddy correlation drag measurements at sea (Deacon, 1973). A similar collation by Wieringa (1974) gives coefficients of 0.87 and 0.048 respectively. For other stability conditions correction can be made, if the air–sea temperature difference and humidity is known, by using Deardorff's (1968) treatment. One proviso attached to estimation via eq. (16) is that the sea surface should be free of substances giving marked catalytic acceleration of the hydration reaction, such as was reported by Berger & Libby (1969) for certain samples of sea-water.

Vertical gradients of carbon dioxide over the sea

The magnitude of the vertical gradient of carbon dioxide in the air over the sea is of interest in assessing the practicability of measuring fluxes at sea by the profile method. From the ratio of the resistance of the air layer z_1 to z_2 to that of the surface viscous sub-layer of water, it follows, for near-neutral conditions and no enhancement of transfer by chemical action, that

$$\frac{N_1 - N_2}{N_s - N_a} = \frac{0.082\, S\alpha \ln(z_2/z_1)}{k(\rho_w/\rho_a)^{1/2}\sigma^{2/3}} \qquad (18)$$

in which the subscripts 1 and 2 refer to heights z_1 and z_2. For a sea temperature of 20 °C and z_1 = 1 m, z_2 = 10 m, this gives a fraction $\sim 2 \times 10^{-4}$. With light wind conditions the hydration reaction should roughly double this value and with stronger winds (say 6–10 m s^{-1}) the radon transfer results also suggest a double value. So under neutral conditions the ratio should be $\sim 5 \times 10^{-4}$ for the wind speed range 2–10 m s^{-1}, provided that catalytic effects are negligible. In regions of strong upwelling $N_s - N_a$ can be of the order of 100 ppm (Keeling, 1968) in which case the 1 to 10 m difference should be of the order of 0.05 ppm; only some 0.02% of the usual $N_a \sim 300$ ppm.

6. The thermal skin layer on the sea

The present treatment can be applied to calculating the temperature difference across the viscous sub-layer on the sea surface for a given heat flux. The calculated values in comparison with observation give some further evidence as to the validity of the formulation for sea conditions.

From eqs. (3) and (5) one obtains the temperature difference, ΔT, between the interface and some small depth z_m as expressed by

$$\Delta T = (u_*/\gamma)^{-1}(Q/C_w)\{\mathrm{Pr}\phi(\mathrm{Pr}) + ak^{-1}\ln(u_* z_m/50\nu\gamma)\} \quad (19)$$

where $\gamma = (\rho_w/\rho_a)^{1/2}$, Q = heat flux, C_w = heat capacity of water per unit volume, and Pr = Prandtl number for sea water (= 7.0 at 20 °C).

For z_m around 30 to 50 cm the logarithmic term in eq. (19) expressing the dimensionless resistance of the fully turbulent water layers is generally less than 25% of $\mathrm{Pr}\phi(\mathrm{Pr})$ and may be neglected for approximate calculations. In that case it reduces to an expression similar in form to that proposed by Saunders (1967). However, Saunders writes λ (= an empirical constant) in place of $\phi(\mathrm{Pr})$. As a result of radiometric measurements of the true surface temperature in the neighbourhood of the Gulf of Maine and estimates of Q, he suggests λ to have a value in the range 5 to 10. Now $\phi(\mathrm{Pr})$ for a water temperature of 20 °C (the average in these trials) has a value of 7.1 (or an effective value of 8.2 taking account of the logarithmic term of eq. (19) with z_m = 30 cm) in satisfactory agreement with the estimate of Saunders. The wind speeds ranged from f2 to f4 on the Beaufort scale (3 to 9 m s^{-1}).

A much more extensive series of observations of ΔT has been treated by Hasse (1971) who also finds satisfactory overall agreement with the Reichardt model of the viscous sub-layer. The variation of the agreement with wind speed can be examined by splitting the results for steady conditions, extracted from the original data (kindly supplied by Professor Hasse), into two groups, one for 4 m wind speed $\leqslant$ 4.8 m s^{-1} and the other above. Occasions of small heat flux (Q < 2 mW cm^{-2}) are rejected. For the rest Q ranged from 2 to 15 mW cm^{-2} (mean 7). From the values of T and Q effective u_* values are calculated from eq. (19) and the geometric means with their standard errors so obtained are:

u_4 m s^{-1}	Mean effective u_*/u_4
1.6 to 4.8, mean 3.6	0.030 ± 19%
4.9 to 9.3, mean 6.4	0.032 ± 21%

The actual values of u_*/u_4 from the analysis by Brocks & Krugermeyer (1970) of wind profiles observed under neutral conditions during the same trials are 0.038 and 0.039 respectively, while the eddy-correlation values of Hasse (1968) give u_*/u_4 = 0.037 ± 10%. The difference between the actual and effective values is not significant and so there is no evidence from these experiments of any great departure from eq. (19) at the higher wind speeds.

7. Discussion

The treatments based on eq. (1) are found to agree quite well with observed rates of transfer in the case of smooth water. However, the sea is rarely smooth and there are large oceanic regions where strong winds and high seas are common. Satisfactory treatment for such conditions will be a matter of great difficulty.

In his early wind tunnel experiments Kanwisher (1963) found the rate of carbon dioxide to water to be approximately proportional to the square of the air speed for the range 3 to 10 m s^{-1}. For non-reactive gases the few results of Liss (1973) and of Hoover & Berkshire (1969) in this range give substantially the same result. Although this may guide expectation as to the variation of air/sea gas transfer with wind speed, as suggested by Kanwisher, a close correspondence is hardly to be expected. However, the radon transfer results of Broecker & Peng (1974), after correction for the 20 °C difference in temperature as between BOMEX and the North Pacific trials, give a wind speed index of $\approx$2.5 which is probably not significantly different from 2.

The increase of u_*/u_{10} with wind speed given by eq. (17) would, if eq. (11) were obeyed, lead to the rate of gas transfer over the range 3–10 m s^{-1} being approximately proportional to $u^{1.1}$. One reason for the actual rate of increase being greater may be sought in fluctuation in thickness of the viscous sub-layer considered in conjunction with the reciprocal relationship between flux and transfer resistance. It has been found by MacIntyre (1971) that the periodic surface dilation produced by capillary ripples is capable of substantially enhancing

the rate of gas transfer through the viscous sub-layer. It is also to be expected that the sub-layer will be thinner over the crests and on the windward slopes of waves than in the troughs. This should be so as the thickness, δ_L, should respond to changing stress in a time of the order of δ_l^2/ν—typically a few milliseconds.

When wave breaking becomes extensive ($u_{10} >$ 10 m s^{-1}) the surface turbulence caused by shear is augmented by splash turbulence, which is a major factor in the dissipation of wave energy. This will doubtless increase transfer via the resulting low resistance patches on the surface of the sea. Spray in the air and bubbles in the water, by increasing the effective area for exchange, will also contribute at high wind speeds.

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9. Appendix

Developing boundary layers and the calculation of u_*

A difficulty in wind tunnel experiments on transfer is to accommodate a long enough surface to give a workable depth (Δ) of boundary layer for profile measurements. The logarithmic range of the wind profile, commonly used in estimating u_*, is only a fraction of Δ. Departure from the logarithmic law commences at $z/\Delta \approx 0.15$ (Hinze, 1959) but no very considerable error is incurred by assuming it to extend to $z/\Delta \approx 0.3$. The growth in Δ with distance x from the upwind edge of a plane surface, smooth or rough, is expressed by

$$\Delta = b(u_*/u_F)\,x$$

in which u_F = free stream velocity and $b \approx 0.3$ according to Monin & Yaglom (1971). For a smooth plate the empirical formula of Schultz-Gronow (Schlichting, 1958) when combined with the above formula gives in terms of the Reynolds number $R_x = u_F x/\nu$:

$$\Delta/x \approx 0.15\,(\log_{10} R_x)^{-1.29}$$

Experiments of Liss (1973)

The wind profiles in these experiments are for a fetch of nearly 4.5 m: at $u_F \sim 3$ m s^{-1} for which the water surface is still smooth, the above formula with $\nu = 0.15$ and $R_x = 9 \times 10^5$ gives $\Delta \approx 7$ cm. The wind speeds at 10 cm above the water surface given by Liss are therefore approximately free stream speeds. This being so and the depth of the boundary layer rather small, it is preferred for the present purpose to calculate u_* for the low speed experiments from eq. (14), i.e. the empirical relationship for smooth surfaces. That this is a justifiable procedure is supported by some observations of Merlivat & Coantic (1975) in experiments in a long wind tunnel giving the relatively deep boundary layer consequent upon a fetch of 34 m over water. The wind profile data for their low speed experiments (nos. 1 and 2) give u_* values in agreement within 10% with those calculated from eq. (2), the well-known relationship established for rigid smooth surfaces.

In calculating the water vapour transfer velocities for the smooth water runs, account is taken of the fact that ψ_m is for $z_m = 10$ cm, which is above the upper limit of the logarithmic range. This is done by obtaining an effective value of z_m for use in eq. (5), as follows. The total non-dimensional resistance of the boundary layer for momentum transfer is u_F/u_*. Subtracting from this the value of r_v for $\sigma = 1$ gives the value of the second term in the denominator of eq. (5) and hence an effective z_m. This is found to be $\approx$8 cm.

Experiments of Möller & Schumann (1970)

In this work wind speeds were measured at four heights (0.5 to 8 cm) at about 2.5 m from the windward end of the water surface. Although the deviations of the profiles from a logarithmic form appear to be small, it is not safe to assume that $du/d(\ln z)$ over such a range gives an accurate u_*. With a water surface the roughness is increasing with distance downwind and this must influence the wind profile form.

The quoted $u_* = 40$ cm s^{-1} for a wind speed of 7.2 m s^{-1} at $z = 3$ cm is only 20% greater than eq. (2) gives for a smooth plate. Furthermore below $u_3 \approx 6$ m s^{-1} the u_* values shown in Fig. 1c of Möller and Schumann are progressively less than for an aerodynamically smooth surface until at $u_3 = 3.6$ m s^{-1} the quoted u_* is only about 50% of the smooth surface value.

An estimate of u_* for the M–S experiments can be made from the results of Francis (1951) who measured the surface stress by the water slope technique. His values for the upwind test section of his water surface, which had a mean fetch of 1.8 m (0.6 to 3.0 m), give $u_* \approx 49$ cm s^{-1} and for a fetch of 2.3 m appropriate to the M–S experiments, interpolation between Francis's upwind and downwind sections increases this to ≈ 53 cm s^{-1}.

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ПЕРЕНОС ГАЗА К ПОВЕРХНОСТИ РАЗДЕЛА ВОЗДУХ-ВОДА И ЧЕРЕЗ НЕЁ

Показано, что рассмотрение, основывающееся на формуле Рейхардта для профиля скорости в турбулентном потоке над гладкой плоской поверхностью, даёт хорошее согласие с опубликованными данными по переносу тепла и массы в пограничном слое в широком интервале чисел Прандтля (или Шмидта) σ. При применении к нереносу к водной поверхности также получено хорошее согласие с опубликованными лабораторными результатами при низких скоростях воздуха (гладкая поверхность воды). Сравнение с наблюдениями на море показывает, что разница невелика между вычисленным коэффициентом испарения и найденным в природе для ветров порядка 7 м/с. Это согласуется с результатами морских измерений, до сих пор показывавших малое увеличение коэффициентов испарения и теплопереноса со скоростью ветра в интервале 4–10 м/с. Перенос нереагирующего газа из воздуха в воду определяется сопротивлением вязкого подслоя воды и рассмотрение в модели гладкой поверхности даёт при этом следующую формулу для скорости переноса V_L:

$$V_L = 0.082\,(\rho_a/\rho_w)^{1/2}\,\sigma^{-2/3}\,u_*$$

где ρ_a/ρ_w-отношение плотностей воздуха и воды, а u_*-скорость трения в потоке воздуха у поверхности. Найдено хорошее согласие между результатами, получаемыми по этой формуле, и опубликованными данными измерений в аэродинамических трубах. При больших скоростях ветра реальный перенос превосходит вычисленные значения и тогда оказывается пропорциональным примерно квадрату скорости ветра.