

ACCOUNTS OF CHEMICAL RESEARCH[®]

AUGUST 1994

Registered in U.S. Patent and Trademark Office; Copyright 1994 by the American Chemical Society

The Theory of Air–Sea Gas Exchange

LEON F. PHILLIPS

Chemistry Department, University of Canterbury, Christchurch, New Zealand

Received February 14, 1994

Introduction

At first sight, the rate of air–sea exchange of a gas such as carbon dioxide appears to be a rather prosaic topic that has acquired some current interest only because of its importance in connection with global warming. This appearance is deceptive. On closer inspection, the theory of air–sea exchange proves to be both complex and interesting, involving as it does considerations of air and sea turbulence, the nature of a liquid surface, and Onsager's irreversible thermodynamics.

Direct experimental measurement of the exchange rate of a trace gas such as CO₂ is very difficult because the exchange rates found in nature are so small. Many so-called measurements of air–sea exchange rates have been based on the assumption of an incorrect rate law, and the few direct, local measurements that have been made have sometimes appeared to be in conflict with sophisticated indirect measurements of globally-averaged rates. On the experimental side, the situation is still highly unsatisfactory and many more direct measurements are needed. Theoretical studies are therefore timely as well as interesting.

Air–sea gas exchange is often described by the equation¹

$$J_g = K_w \alpha (P_{\text{air}} - P_{\text{sea}}) \quad (1)$$

where J_g is the gas flux into the sea, α is the solubility of the gas at the sea temperature, and P_{air} and P_{sea} are the partial pressure of the gas in the air and the pressure in equilibrium with bulk seawater, respec-

tively. The quantity $\alpha(P_{\text{air}} - P_{\text{sea}})$ is approximately the difference between the surface concentration and the bulk concentration in the liquid. The empirical quantity K_w is called the transfer velocity, or "piston velocity", and the product of transfer velocity and solubility is supposed to be a function only of wind speed.² Equation 1 is best regarded as a definition of the transfer velocity K_w . As we shall see, it does not provide a reliable means of determining the flux J_g , although it has been used for this purpose.

The most obvious deficiency of eq 1 is that it does not include any dependence of gas flux on the temperature difference across the air–sea interface, whereas it seems clear that, at least in the steady state, the fluxes of heat and matter should be coupled³ through a "heat of transport" which should be related to the heat of solution of a gas such as CO₂, or to the heat of condensation in the case of water vapor. Thus it is no surprise to find that measured values of transfer velocity for CO₂ prove *not* to be a function of wind speed alone, the range of measured values at a typical "global-average" wind speed of 8 m s⁻¹ amounting to a factor of 5. The use of oceanographic data based on eq 1 leads to serious problems with the earth's annual budget for anthropogenic CO₂, the fluxes derived from eq 1 giving too small a value for the oceanic sink; also, the observed interhemisphere concentration gradient of CO₂ is too small to be compatible with the resulting need for most CO₂ generated in the northern hemisphere to travel to the southern oceans in order to be absorbed.⁴ Efforts to

(1) Liss, P. S.; Merlivat, L. Air-sea gas exchange rates: introduction and synthesis. In *The Role of Air-Sea Exchange in Geochemical Cycling*; Buat-Menard, P., Ed.; D. Reidel: Dordrecht, 1986; pp 113–127.

(2) Etcheto, J.; Boutin, J.; Merlivat, L. Seasonal variation of the CO₂ exchange coefficient over the global ocean using satellite wind speed measurements. *Tellus* **1991**, *43B*, 247–255.

(3) Denbigh, K. G. *The Thermodynamics of the Steady State*; Methuen: London, 1951; p 71.

Leon Phillips is a New Zealander who was educated at the University of Canterbury (M.Sc.) and Cambridge University (Ph.D., Sc.D.). He has been a faculty member at Canterbury since 1961 and a full professor since 1966. His research involves experimental and theoretical studies of the kinetics, photochemistry, and dynamics of small molecules, especially in relation to planetary atmospheres.

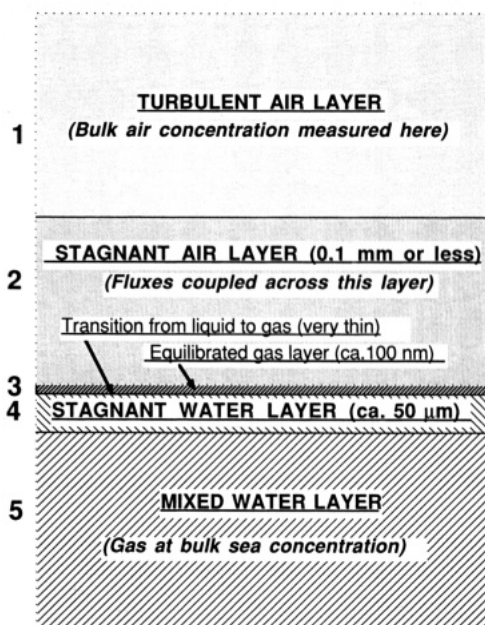


Figure 1. Model used for calculations of air-sea exchange rates. The results shown in Figures 2–6 relate to a simplified model in which the turbulent air layer is replaced by a mixed layer of constant composition.

retrieve this situation without discarding eq 1 are summarized elsewhere.^{5–7}

The Theoretical Model

The model of the air–sea system used here is shown in Figure 1. It comprises (1) a thick layer of turbulent air within which bulk values of concentration and temperature are measured and in which temperature and concentration profiles are quasilogarithmic (see eq 5); (2) a thin (<ca. 0.1 mm) layer of stagnant air adjacent to the liquid, in which profiles of temperature and composition are linear; (3) the liquid surface itself, plus an adjacent film of gas which is in equilibrium with the liquid and whose thickness is of the order of 1 mean free path for water vapor in air at atmospheric pressure (ca. 100 nm); (4) a thin liquid layer (10–50 μm) which provides the main resistance to transport for a sparingly-soluble gas such as CO_2 and in which temperature and composition profiles are linear for a steady-state model and *erfc* functions of distance for a surface-renewal model; and (5) a thick layer of the bulk liquid composition, as maintained by turbulent mixing and/or chemical reaction (pH of seawater \approx 8.2). Coupling of heat and matter fluxes, in the sense of irreversible thermodynamics, occurs across the stagnant air layer, because the gas immediately adjacent to the surface is in equilibrium with the liquid. In the steady state, transfer of gas across the stagnant layer to the side adjacent to the liquid results in release of the heat of solution or condensation. The location of the irreversible process in the stagnant gas layer, and the relationship of the heat of solution or

condensation to the heat of transport, can be demonstrated by treating transport through the gas–liquid interface as a limiting case of thermoosmosis through a membrane.⁸

One of the conclusions that emerge from numerical calculations for this model is that the local temperature at the liquid surface plays a critical part in deciding the magnitude and sometimes even the direction of the flux of a gas such as CO_2 . Because of the temperature dependence of solubility, the surface temperature controls the ratio between gas pressure and dissolved concentration at the surface, and so controls the concentration gradient in the liquid. As noted above, diffusion through the layer of liquid immediately below the surface presents the main resistance to gas transfer for a gas such as CO_2 (here we do not consider very reactive gases, such as NH_3 , for which this is not true in general). In the steady state, concentration gradients throughout the model must adjust themselves so that the local flux matches the flux through the top layer of liquid.

For calculations whose results are to be compared with experimental data it is necessary to include every feature of the model in Figure 1. For calculations aimed at providing a qualitative understanding of the effects of varying such parameters as stagnant layer thickness, air temperature, or relative humidity, it is sufficient to use a simpler model, in which the turbulent air layer is replaced by a mixed layer of constant composition located immediately above the stagnant layer. Fortran listings and input data files for computer programs used in this work can be obtained by e-mail from phillips@chem.canterbury.ac.nz.

Irreversible Thermodynamics

A simple derivation based on Denbigh's treatment³ of thermal diffusion through a membrane leads to the following expression for the flux J_g through the stagnant air layer:^{9,10}

$$J_g = -D_{gm} C_{gm} [(Q_g^*/RT_m) T_m'/T_m + C_{gm}'/C_{gm}] \quad (2)$$

where the subscript *g* identifies the gas involved, a subscript *m* indicates a gas-phase value measured at the liquid surface, a prime denotes a derivative with respect to height *z*, D_g is the diffusion coefficient, C_g is concentration, Q_g^* is the "heat of transport" given by

$$Q_g^* = Q_g - C_p T_m \quad (3)$$

where Q_g is the heat of solution or condensation of the gas whose heat capacity is C_p , and the other symbols have their usual meanings. Equation 2 is a convenient form for use in numerical calculations. In the absence of a temperature gradient it reduces to Fick's law of diffusion. Note that, because this equation is applied to transport across the stagnant air layer, the quantities which appear are all gas-phase values and

(4) Tans, P. P.; Fung, I. Y.; Takahashi, T. Observational constraints on the global atmospheric CO_2 budget. *Science* **1990**, *247*, 1431–1438.

(5) Erickson, D. J., III. A stability-dependent theory for air-sea gas exchange. *J. Geophys. Res.* **1993**, *98*, 8471–8488.

(6) Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **1992**, *97*, 7373–7382.

(7) Phillips, L. F. The physical chemistry of air-sea gas exchange. Workshop on the sea-surface microlayer and its potential role in global change, University of Rhode Island, 1994, to be published.

(8) Phillips, L. F. Steady-state thermodynamics of transfer through a gas-liquid interface, treated as a limiting case of thermo-osmosis. *Chem. Phys. Lett.*, submitted.

(9) Phillips, L. F. CO_2 transport at the air-sea interface: effect of coupling of heat and matter fluxes. *Geophys. Res. Lett.* **1991**, *18*, 1221–1224.

(10) Phillips, L. F. Steady-state heat and matter exchange at a phase interface. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2187–2191.

Table 1. Values of C_p , Q , Q^* , and Q^*/RT for Some Typical Solute Gases^a

gas	$C_p/\text{J K}^{-1} \text{mol}^{-1}$	$Q/\text{kJ mol}^{-1}$	Q^*	Q^*/RT
He	20.8	0.75	-5.3	-2.2
H ₂	28.8	3.8	-4.6	-1.9
SF ₆	97.2	25.5	-2.7	-1.1
CH ₄	35.7	13.1	2.7	1.1
O ₂	29.4	13.4	4.9	2.0
NO	29.9	13.7	5.0	2.1
Ar	20.8	13.6	7.6	3.2
CO ₂	37.1	20.5	9.7	4.0
N ₂ O	38.7	23.0	11.8	4.9
SO ₂	39.8	25.9	14.4	6.0
Rn	20.8	22.9	16.9	7.0
NH ₃	35.6	29.5	19.2	8.0
H ₂ O	33.6	44.0	34.3	14.2

^a $T = 290 \text{ K}$; $RT = 2.41 \text{ kJ mol}^{-1}$.

it is not necessary to deal directly with the difficult region where the medium is changing rapidly from liquid to gas. In order to compare the results of the present calculations with ones more closely related to eq 1, where temperature effects are neglected, the value of Q_g^* can be set equal to 0 in eq 2 (but note that this eliminates both the coupling of heat and matter fluxes via Q_g and the temperature-dependent part of the chemical potential gradient which is responsible for diffusion). The heat of transport which is involved in transfer across a phase interface is larger by several orders of magnitude than the analogous quantities which appear in connection with such phenomena as thermoosmosis, and it seems likely that the thermodynamics of the steady state has its most striking application in this kind of process.

Equation 3 shows that the heat of transport is dependent on both the nature of the gas and the temperature. Table 1 gives values of Q_g , C_p , Q_g^* , and Q_g^*/RT for a number of gases at a typical sea temperature.¹⁰ The ratio Q_g^*/RT governs the relative importance of the temperature gradient and the concentration gradient in the expression for the flux. The existence of these large differences between Q_g^* values for different gases implies that care must be exercised in inferring the flux of one gas from the measured flux of another, as has often been done in the past.

Simple Model Calculations

A number of numerical calculations^{7,11} have been made using a simplified version of the model in Figure 1 without the turbulent air layer, in the framework of the Higbie–Danckwerts surface-renewal model,¹² with the aim of understanding the qualitative dependence of the gas flux on the parameters of the model. Adjustable parameters in these calculations were the air temperature and dew point, bulk sea temperature, stagnant layer thickness, air and sea concentrations of CO₂, the surface renewal time τ , and the intensity of long-wavelength infrared radiation. In the surface-renewal model, the surface is regarded as a mosaic of elements of different ages, individual elements being replaced by fresh surface at irregular intervals. We define the renewal time τ as the reciprocal of the

(11) Phillips, L. F. CO₂ transport at the air–sea interface: numerical calculations for a surface-renewal model with coupled fluxes. *Geophys. Res. Lett.* **1992**, *19*, 1667–1670.

(12) Danckwerts, P. V. *Gas-liquid Reactions*; McGraw-Hill: New York, 1970.

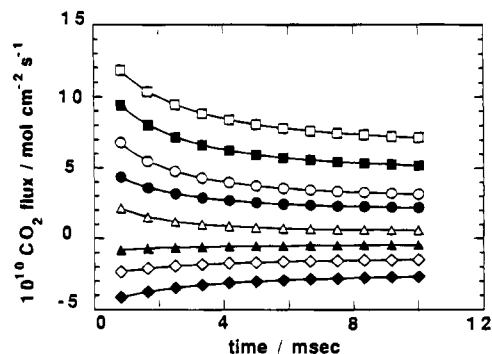


Figure 2. Calculated air–sea CO₂ flux as a function of surface renewal time for fixed air and sea partial pressures of CO₂ (4.0 and 3.6×10^{-4} atm) and bulk sea temperature (288 K), with an extremely thin stagnant air layer (4×10^{-5} cm). Values of air temperature and dew point (K) for individual curves, reading from top to bottom: (278, 278), (288, 278), (298, 278), (288, 288), (298, 288), (278, 298), (288, 298), (298, 298).

fraction f of the surface which is renewed in unit time, the distribution of ages t being given by

$$p(t) = \text{constant} \times t^{-1} \exp(-ft) \quad (4)$$

where the value of the constant is fixed by normalizing the total probability to unity. The conclusions to be drawn from these calculations are not dependent on the surface-renewal model, which merely provides a convenient framework for the calculations. Also, since these are model calculations, designed to reveal gross effects, the ranges of values of such parameters as the dew point need not be limited to typical values found in nature.

Figure 2 shows the dependence of flux on renewal time for various combinations of air temperature, as measured at the top of the stagnant air layer, and dew point, for fixed air and sea partial pressures of CO₂ (4.0 and 3.6×10^{-4} atm), fixed sea temperature (288 K), and fixed stagnant air-layer thickness (400 nm). This is a very thin stagnant layer, so heat conduction through the stagnant layer has a marked effect on the surface temperature T_m . Higher fluxes are found for shorter renewal times, corresponding to higher wind speed and greater wave activity. A notable feature of the results in Figure 2 is that, although the flux is expected to be positive (into the sea) on the basis of the air–sea partial pressure difference, the flux becomes negative when the surface is strongly heated either by conduction across the stagnant layer or by condensation of water vapor. This provides an explanation for the otherwise inexplicable observation, in eddy correlation studies,^{13,14} of CO₂ fluxes opposed to the air–sea partial pressure difference. The effect of heat conduction across the stagnant layer disappears for a thick stagnant layer unless the renewal time is very long, but the effect of evaporation or condensation of water remains. This *kinetic* coupling between the fluxes of water vapor and CO₂ (or other trace gas) can cause the flux of CO₂ to occur in the direction opposite

(13) Smith, S. D.; Jones, E. P. Evidence for wind-pumping of air–sea gas exchange based on direct measurements of CO₂ fluxes. *J. Geophys. Res.* **1985**, *90*, 869–875; Isotopic and micrometeorological ocean CO₂ fluxes: different time and space scales. *J. Geophys. Res.* **1986**, *91*, 10529–10532.

(14) Smith, S. D.; Anderson, R. J.; Jones, E. P.; Desjardins, R. L.; Moore, R. M.; Hertzman, O.; Johnson, B. D. A new measurement of CO₂ eddy flux in the near-shore atmospheric surface layer. *J. Geophys. Res.* **1991**, *96*, 8881–8887.

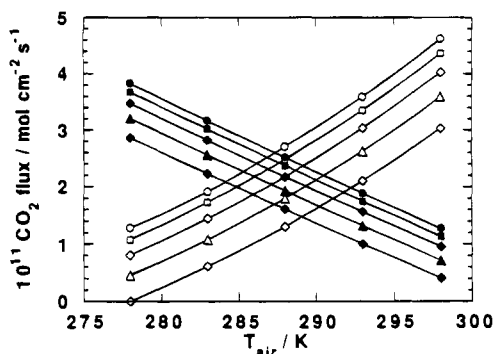


Figure 3. Air-sea CO_2 flux as a function of air temperature for a renewal time of 1 s, air and sea partial pressures of CO_2 equal to 4.0 and 3.6×10^{-4} atm, respectively, bulk sea temperature 288 K, and stagnant air layer thickness 10^{-2} cm. Filled points have Q^* set to 0. Dew-point temperatures, reading from top to bottom: 278, 283, 288, 293, and 298 K.

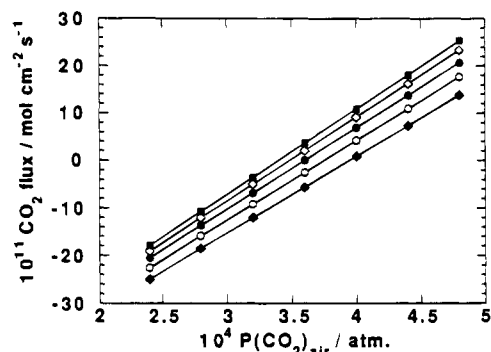


Figure 4. Air-sea CO_2 flux as a function of the partial pressure of CO_2 in air, for fixed sea partial pressure (3.6×10^{-4} atm) and fixed air and sea temperatures (both 288 K). Renewal time 0.1 s; stagnant layer thickness 10^{-3} cm. Lines correspond to dew-point temperatures of 278, 283, 288, 293, and 298 K, reading from top to bottom.

to the thermodynamic driving force for transport of CO_2 alone, an effect which is reminiscent of active transport in biological systems.

Figure 3 shows the variation of flux with air temperature, for a thicker stagnant air layer, for the same CO_2 partial pressures and sea temperature as in Figure 2, with a range of dew-point temperatures. In this figure, filled points have Q^* set to 0, which turns off the effect of irreversible thermodynamic coupling of the heat and matter fluxes. For the filled points, increasing the air temperature decreases the gas flux because of heating of the surface by conduction through the thick stagnant layer. For the unfilled points, increasing the air temperature increases the flux because the effect of the term involving the temperature gradient in eq 2 predominates.

Figure 4 shows that the calculated flux varies linearly with the partial pressure difference across the interface, but is not proportional to the partial pressure difference, as implied by eq 1, unless the air and sea temperatures and the dew point are all equal. Figure 5 shows that the flux is independent of stagnant layer thickness for values up to about 0.1 mm when there are no temperature effects. This is because, as mentioned earlier, the main resistance to gas transfer occurs in the top few microns, or tens of microns, of liquid. If the temperatures (including the dew point) are not all the same, varying the stagnant layer thickness does make a difference, as shown in

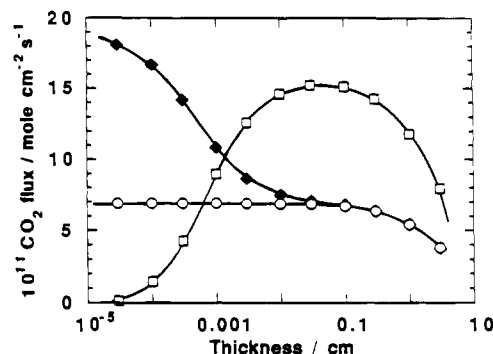


Figure 5. Air-sea CO_2 flux as a function of the thickness of the stagnant air layer, for renewal time 0.1 s, air and sea partial pressures of CO_2 4.0 and 3.6×10^{-4} atm, respectively, and bulk sea temperature 288 K. Unfilled circles: air temperature and dew point both 288 K. Filled diamonds: dew point 278 K, air temperature 288 K. Unfilled squares: air temperature 298 K, dew point 288 K.

Figure 5, because of its effect on heat conduction and/or water vapor transport through the stagnant layer.

Radiometric observations of the sea surface show that heat losses by emission of long-wavelength radiation are typically of the order of a few hundred watts per square meter under clear-sky conditions.¹⁵ Such losses are of similar magnitude to the usual sensible (conductive plus convective) heat losses, and the mean distance for falloff of intensity with depth can be as short as $10 \mu\text{m}$,¹⁶ which is of the same order of magnitude as the thickness of the water layer that provides the main resistance to the gas flux. It is clear that the infrared emission must contribute to maintenance of the "cool skin" on the surface of the ocean¹⁷ and, therefore, might have a significant effect on the flux of a gas such as CO_2 . Figure 6 shows the dependence of the calculated CO_2 flux on sea-surface temperature for conditions which are close to typical ocean conditions.¹⁸ For the data in this figure, the sea-surface temperature was varied either by varying the dew point of the air (unfilled circles) or by varying the intensity of long-wavelength infrared radiation (filled circles). The effect of varying the intensity of the infrared radiation is seen to be quite small relative to the effect of varying humidity, a result which can be rationalized in terms of the latent heat of vaporization being absorbed or released right at the surface of the liquid, whereas the infrared radiation is absorbed or emitted over a range of depths which, although small, is not negligible.

Calculations with a Turbulent Air Layer

Time-averaged vertical profiles of intensive variables q through a turbulent boundary layer are of the quasi-logarithmic form:

(15) Schlüssel, P.; Emery, W. J.; Grassl, H.; Mammen, T. C. On the bulk-skin temperature difference and its impact on satellite remote sensing of the sea surface temperature. *J. Geophys. Res.* **1990**, *95*, 13341-13356.

(16) Schlüssel, P. Personal communication.

(17) Katsaros, K. B. The aqueous thermal boundary layer. *Boundary-Layer Meteorol.* **1980**, *18*, 107-127.

(18) Phillips, L. F. CO_2 transport at the air-sea interface: effect of radiative cooling on temperature profiles and gas fluxes. *Geophys. Res. Lett.*, submitted.

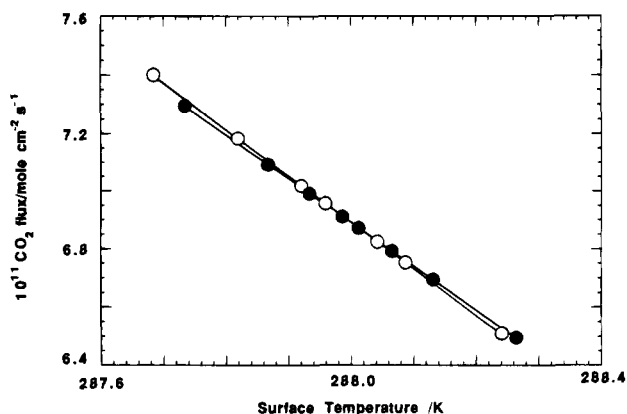


Figure 6. Variation of calculated CO_2 flux with sea-surface temperature, the surface temperature being varied either by changing the dew point of the air (unfilled circles) or by varying the intensity of radiation (filled circles). Air and sea temperatures both 288 K, air and sea partial pressures of CO_2 3.6 and 3.2×10^{-4} atm, surface renewal time 0.1 s, thickness of stagnant air layer 0.1 mm. Filled circles are for dew point 288 K and integrated radiative fluxes $-2000, -1000, -500, -100, 100, 500, 1000,$ and 2000 W/m^2 , reading from left to right on the plot. Unfilled circles, zero radiation flux and dew-point temperatures of 278, 283, 286, 287, 289, 290, and 293 K, reading from left to right.

$$\frac{q - q_0}{q^*} = \frac{1}{k_a} \left[\text{Ln} \left(\frac{z}{z_0} \right) - \psi \left(\frac{z}{L} \right) \right] \quad (5)$$

where q is temperature or concentration at height z , q_0 is the value at height z_0 , where z_0 is a parameter called the “roughness length” (essentially the minimum eddy size), q^* is $-\text{flux}/u^*$, or $-\text{flux}/\rho\sigma u^*$ when $q = T$, u^* is the “friction velocity” (independent of z), $\rho\sigma$ is the product of density and specific heat for air, k_a ($=0.4$) is Von Karman’s constant, ψ is a stability function whose form depends on whether the temperature profile is stable (temperature increasing with height) or unstable, and L is the Monin–Obukov length,¹⁹ all of which helps us to understand why Werner Heisenberg gave up working on turbulence and invented quantum mechanics instead.²⁰ Equation 5 holds in the turbulent layer provided $-z/L > \approx 2$.

The eddy diffusion coefficient or eddy thermal diffusivity D_q^* is given as a function of height z by

$$D_q^* = k_a u^* z / \phi(z) \quad (6)$$

where ϕ is another stability function, closely related to ψ . We can define a transition height z_{1q} as the height at which D_q^* equals the molecular diffusion coefficient (or thermal diffusivity = thermal conductivity divided by $\rho\sigma$) for the flux associated with intensive variable q , and write q_1 for the value of q (temperature or concentration) at height z_{1q} .

The initial motivation for the calculations with turbulence included was a desire to avoid having to consider the effects on the gas flux of such variables as wind speed, nature of the wave field, or degree of surface contamination, and to obtain the gas flux by scaling it to the heat flux in the water, the environmental factors being assumed to affect both fluxes to the same extent. The first step in such a calculation would be to obtain the surface temperature T_m from

the measured air and sea temperatures together with experimental values of the sensible heat and water vapor fluxes. This could be done in principle by using eq 5 to calculate the temperature T_1 at the height z_{1T} obtained from eq 6, and then using the value of z_{1T} together with the known temperature gradient (calculated from the conductive heat flux through the stagnant layer and the thermal conductivity of air) to calculate the surface temperature T_m . Once the surface temperature is known, this fixes the surface value of the solubility α , which in turn fixes the ratio of liquid- and gas-phase concentrations at the surface. Given the surface temperature, it therefore becomes possible to calculate the flux of the trace gas by scaling the dissolved gas flux, via the ratio of thermal and molecular diffusivities, to the heat flux in the liquid layer immediately below the surface, and then adjusting the surface concentration iteratively until the gas flux is the same on both sides of the interface. Thus, in principle, it should be possible to calculate the CO_2 flux from a knowledge of the heat and water vapor fluxes and the bulk air and water temperatures and concentrations, together with u^* and the known functions ψ and ϕ .

Unfortunately, the above procedure does not work in practice, at least with the available experimental data, because the extrapolation to z_{1T} using eq 5 is nearly always too long to yield an accurate value of T_1 , and both a different approach and a revised objective are needed. The alternative approach that has been adopted²¹ is to calculate the theoretical transfer velocity for a range of values of surface temperature T_m and to use measured values of transfer velocity to select the best value of T_m , and then to use this value of surface temperature to calculate the corresponding values of temperature and water vapor concentration at the transition heights z_{1T} and z_{1w} . These transition values are of no particular interest for their own sake, but they do provide useful criteria for deciding that a calculation has failed, as is deemed to have happened when the calculated value of water vapor concentration at z_{1w} is negative, or when the value of T_1 is outside the range between T_m and the air temperature T_a by more than some arbitrary amount (normally 3 K). The value of this type of calculation, and the basis of the revised objective, is that it provides the route to an experimental demonstration of the correctness of eq 2, as opposed to an alternative treatment²² in which the quantity corresponding to Q^* is much smaller than the values given in Table 1 and of opposite sign. The details of the calculation are given elsewhere;²¹ here we consider only the results.

Of the many measurements of gas–water exchange rates in the literature, three have been found in which the fluxes of heat and water vapor were also measured. These are the laboratory measurements of oxygen exchange, in a wind tunnel, by Liss et al.,²³ and the field measurements of CO_2 exchange, using the eddy-correlation method, by Smith and co-work-

(21) Phillips, L. F. Experimental demonstration of coupling of heat and matter fluxes at a gas–liquid interface. *J. Geophys. Res.*, in press.

(22) Doney, S. C. Irreversible thermodynamic coupling between heat and matter fluxes across a gas–liquid interface. *J. Chem. Soc., Faraday Trans.*, in press.

(23) Liss, P. S.; Balls, P. W.; Martinelli, F. N.; Coantic, M. The effect of evaporation and condensation on gas transfer across an air–water interface. *Oceanol. Acta* 1981, 4, 129–138.

(19) Panofsky, H. A.; Dutton, J. A. *Atmospheric Turbulence*; John Wiley & Sons: New York, 1984.

(20) Born, M. *My Life*; Taylor and Francis: London, 1978; p 211.

Table 2. Calculated Surface Temperature (T_m) and Transition Temperature (T_1) To Fit Data of Liss et al.,¹² Assuming Ordinary Diffusion and Linear Profiles of Temperature and Concentration on the Sea Side of the Interface

run	T_a	T_s	dew pt	K_w^a	T_m	T_1	notes ^b
1	288.25	288.05	283.85	1.89	287.705	285.862	5
2	286.95	287.35	283.85	2.02	287.090	285.722	3, 5
3	299.55	288.35	291.85	1.78	289.318	291.680	1, 4, 6
4	299.75	288.25	292.55	1.90	289.249	291.621	1, 4, 6
5	279.95	288.25	278.05	2.01	286.284	285.123	2, 4
6	280.95	287.45	278.25	2.02	285.781	284.870	2, 4
7	287.45	289.05	287.15	2.06	288.671	288.689	2, 4, 5
8	294.95	288.25	293.75	1.72	290.155	291.452	1
9	298.15	288.75	296.75	1.59	292.001	293.859	1
10	281.65	287.55	279.45	3.04	285.211	284.547	2, 4
11	284.55	287.85	283.95	2.92	286.476	285.997	2, 4
12	287.95	288.15	287.15	2.96	287.977	288.736	5
13	297.15	287.65	291.75	2.57	290.261	292.336	1
14	301.45	287.45	294.75	2.31	292.164	295.006	1
15	302.35	287.95	296.25	2.10	293.840	296.920	1
16	298.35	286.95	295.75	3.02	291.499	293.510	1
17	282.95	288.05	280.95	11.3	287.186	286.322	2, 4
18	281.95	287.75	280.65	9.10	286.636	285.581	2, 4
19	288.75	288.45	288.95	10.3	288.535	288.609	2
20	287.95	287.35	288.85	9.18	287.571	287.402	1, 5
21	305.05	286.95	296.15	5.45	291.137	294.399	1
22	303.15	288.05	297.85	6.45	291.509	293.826	1
23	301.05	287.65	296.95	7.29	290.582	293.379	1
24	282.55	287.15	281.85	26.6	286.737	285.555	2, 4
25	284.25	288.25	283.75	23.5	287.825	286.918	2, 4
26	288.25	288.15	288.15	25.6	288.153	288.160	1, 4
27	300.15	289.45	293.25	23.2	290.178	291.879	1, 4
28	296.85	288.25	296.05	24.8	289.187	291.303	1, 4
29	283.55	288.45	282.95	38.2	288.049	286.721	2, 4
30	288.35	288.35	288.75	37.9			7
31	302.35	289.25	295.95	38.4	290.047	291.898	1, 4

^a Units of K_w , cm/h. ^b Notes: (1) Cannot calculate T_1 without flux coupling for water. (2) Cannot reproduce K_w without flux coupling for oxygen. (3) Cannot reproduce K_w exactly with ordinary diffusion and linear profiles. (4) Can reproduce K_w with an *erfc* profile on the water side of the interface. (5) The calculated value of T_1 does not lie between T_a and T_m . (6) Equation 6 gives a negative value of z_{1q} ; put $z_{1q} = z_{1T}$. (7) T values inconsistent with water vapor flux.

ers.^{13,14} The data of Liss et al. were obtained from a well-controlled series of experiments, under a wide range of conditions. Results of the present calculations for their data are given in Table 2. The first column of the table gives the run number assigned by Liss et al., and the next four columns give the experimental values of air temperature, water temperature, dew point, and measured transfer velocity K_w , widely different transfer velocities generally corresponding to different wind speeds. The following two columns give the calculated values of surface temperature T_m and transition temperature T_1 which correspond most closely to the experimental value of transfer velocity, and the final column contains codes which relate to the success or failure of the calculation with and without various options in effect. The options available are (i) turning off flux coupling (by setting Q^* to 0) for water vapor alone or for both water vapor and the gas being transferred, in this case O_2 ; (ii) assuming concentration and temperature profiles of the form

$$q(z) = q_s + (q_m - q_s)erfc(z/2(Dt)^{1/2}) \quad (7)$$

on the water side of the interface instead of linear profiles, where z is now measured *into* the water, a

subscript s denotes a bulk value in the water, and t is an average surface-renewal time, where linear profiles are appropriate for a steady-state model and the profile in eq 7 is appropriate for a surface-renewal model; and (iii) assuming eddy diffusion instead of ordinary diffusion on the water side of the interface, where the diffusion coefficient and the thermal diffusivity become equal when transport is by turbulent mixing (as would be the case, for example, in a surf zone) and the scaling of the gas flux to the heat flux means that actual values of liquid-phase eddy-diffusion coefficients do not enter the calculation.

The following points can be made about the results in Table 2:

(1) With the exception of the values from two runs (runs 2 and 30) all of the experimental values of transfer velocity can be reproduced exactly on the basis of the present theory with flux coupling turned on (Q^* given by eq 3) for both water vapor and oxygen, with ordinary diffusion rather than eddy diffusion on the water side of the interface, with linear rather than *erfc* profiles on the water side of the interface, and with the definition of transition height z_{1q} as the height at which eddy and molecular diffusion coefficients are equal. For run 30, the sensible heat flux was zero and the air and water temperatures were the same (15.2 °C) and below the dew point of the air (15.6 °C), which is incompatible with the negative value reported for the water vapor flux, so no calculation was possible (note 7). For run 2 it is not possible to duplicate the experimental value of transfer velocity with any combinations of options in effect (note 3), and it seems plausible to invoke experimental error as the source of the difficulty.

(2) For many of the experiments (runs 3, 4, 8, 9, 13–16, 20–23, 26–28, 31), including most of those in which there was a sizable gas–water temperature difference, it was not possible to calculate the temperature and water vapor transition values T_1 and w_1 successfully with flux coupling turned off (Q^* set to 0) for water vapor (note 1), and there are no runs for which the calculation of T_1 and w_1 failed with flux coupling turned on for water vapor.

(3) For most of the remaining experiments (runs 5–7, 10, 11, 17–19, 24, 25, 29), although the calculation of T_1 was successful with Q^* set to 0 for water vapor, it still was not possible to duplicate the experimental value of transfer velocity without including flux coupling for oxygen (note 2). In combination with the previous point, this makes it clear that coupling of heat and matter fluxes, in the sense of Onsager's irreversible thermodynamics, must be included in any theoretical treatment of steady-state gas–liquid transfer.

(4) For about half of the experiments (runs 3–7, 10, 11, 17, 18, 24–29, 31) it was possible to reproduce the experimental values of transfer velocity with the assumption of *erfc* profiles on the water side of the interface, but there were no runs for which an *erfc* profile was required by the data. Thus a steady-state model is favored over a surface-renewal model for this experimental system.

(5) There were no runs for which the experimental value of transfer velocity could be reproduced with the assumption of eddy diffusion instead of ordinary molecular diffusion on the water side of the interface.

(6) For five of the experiments (runs 1, 2, 7, 12, 20) the calculated value of T_1 does not lie between the surface temperature and the bulk air temperature T_a . For all of these runs the gas-water temperature difference was rather small and the calculation of T_1 likely to be less accurate than usual, and for run 2 there was a prior assumption of experimental error.

(7) The best value of surface temperature T_m is often strikingly different from the bulk water temperature. Extreme cases are run 16, in which the surface was heated by nearly 6 K, and run 10, in which the surface was cooled by more than 2 K. As noted above, heating the surface tends to reduce the gas flux into the water and cooling the surface tends to increase it.

The field measurements of Smith and co-workers^{13,14} are necessarily less well controlled than the above wind-tunnel studies. Nevertheless, as discussed elsewhere,²¹ they also support the present theory with inclusion of coupling of heat and matter fluxes. The main point of difference with the wind-tunnel data is that the results of Smith and co-workers tend to favor eddy diffusion rather than ordinary molecular diffusion on the sea side of the interface. This is consistent with earlier suggestions that their measurements, which were made close to shore, were affected by proximity to a surf zone.

Conclusions

The present theory is in excellent agreement with the best available experimental data and appears potentially capable of providing a solution to the difficulties which have arisen from the use of eq 1. The theory also suggests a new method of determining air-sea fluxes of trace gases, a method which is likely to be much easier to put into effect than eddy correlation. There are two versions of this method. In the

first, the profiles of temperature and composition through the turbulent layer are determined with sufficient precision to enable the surface temperature to be found with an accuracy of the order of ± 0.01 °C. The calculation of the trace gas flux from the bulk concentrations and temperatures and the total heat flux is then straightforward. (An accuracy of the order of ± 0.01 °C is required because the calculated transfer velocity typically varies by a few percent for a 0.01 °C change in surface temperature. The best measurements of temperature profiles through the sea surface made so far^{15,23-26} are about an order of magnitude less precise than this.) In the second version, the surface temperature T_m is obtained either directly, by some method (perhaps spectroscopic) which has still to be devised, or indirectly, by measuring the flux of another gas such as oxygen and choosing the value of surface temperature which corresponds to the measured flux. At present, this indirect approach to determining T_m appears likely to be more fruitful.

I am grateful to Dr. Pieter Tans for helpful discussions and to Dr. Stuart Smith for instructive correspondence on the subject of atmospheric turbulence. Much of the work described in this Account was carried out at the National Center for Atmospheric Research in Boulder, CO. The hospitality of NCAR and support by the Visiting Scientist Program of the Atmospheric Chemistry Division are gratefully acknowledged. NCAR is sponsored by the National Science Foundation.

(24) Azizyan, G. V.; Volkov, Yu. A.; Solov'yev, A. V. Experimental investigation of thermal structure of thin boundary layers of the atmosphere and over ocean. *Izv., Atmos. Ocean. Phys.* **1984**, *20*, 482-488.

(25) Volkov, Yu. A.; Solov'yev, A. V. Vertical structure of the temperature field in the atmospheric layer near the surface of the ocean. *Izv., Atmos. Ocean. Phys.* **1986**, *22*, 697-700.

(26) Mammen, T. C.; Von Bosse, N. STEP—a temperature profiler for measuring the oceanic thermal boundary layer at the ocean-air interface. *J. Atmos. Ocean. Technol.* **1990**, *7*, 312-322.