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Effects of Hydration on Carbon Dioxide Exchange across an Air-Water Interface

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The rate of dissolved $C^{14}O_2$ depletion from a thermally regulated water tank situated in a controlled-speed wind tunnel was monitored to determine the rate constant for interphase CO_2 exchange as a function of air speed and solution pH . The results appear to support the long proposed concept of a layer of laminar (nonturbulent) flow on the surface of bodies of water exposed to wind stress. The CO_2 exchange rate for a solution pH in the 6.5 region (where CO_2 can react with water and hydroxyl ions to a significant extent) was found to be greater than the rate in the $pH < 4$ region (where CO_2 effectively acts as an inert gas) by an amount that closely matched theoretical expectations based on the stable-layer diffusion model. When the surface layer was thicker than 0.20 mm (which corresponded to air speeds under 4 m/sec) and the solution pH was greater than 6.0, there was evidence that a net bicarbonate- CO_2 conversion, caused by the molecular CO_2 diffusion gradient, took place in the layer and that this conversion was responsible for an increase in the rate of carbon dioxide exchange. Under certain conditions, this unique surface layer reactivity may allow carbon dioxide to be exchanged between the atmosphere and hydrosphere more rapidly than if it were a nonreactive gas.

INTRODUCTION

The exchange of gases between phases is critical to many areas of environmental research. There is at present no comprehensive theory whereby the specific rate of exchange for a particular gas can be predicted from the physical characteristics of a system. The exchange mechanism for any specific gas may indeed vary with the environmental conditions under which it is observed. The present study has established a workable exchange model for carbon dioxide in a wind-water tunnel environment and has used this model to make accurate predictions describing the pH dependence of the carbon dioxide exchange rate.

INTERPHASE GAS EXCHANGE MODELS

Measurements of gaseous exchange between phases are customarily discussed in terms of an 'exchange constant' which describes the rate of net mass exchange as a function of the concentration difference between the two phases.

This empirical constant k is defined by the following relationship:

$$dq/dt = kA(C_1 - C_2) \quad (1)$$

In this expression q has units of quantity, t denotes time, k is the exchange constant in units of length/time, A is the area of the interface, and C_1 and C_2 represent the concentration in quantity/unit-volume for the two phases. The rate of net mass exchange is thus a function of the concentration difference, the interface area, and the empirical constant k .

The physical significance of the constant k is subject to various interpretations, depending on the physical model chosen to describe the exchange mechanism. In the best known model [Lewis and Whitman, 1924] a liquid film at the surface is assumed to be in locally laminar or streamline flow, whereas the main body of the liquid is in turbulent flow with complete mixing. Similar assumptions are made for the gas phase. Gaseous exchange across the two interfacial layers is thought to be regulated by molecular diffusion, with the approximately 10^4 times slower diffusion in the liquid phase being the rate controlling phenomenon [Bolin, 1960].

In the laminar layer model the exchange constant k is resolved into the ratio of the molecular diffusivity D in the liquid layer to

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the thickness δ of the layer.

$$k = D/\delta \quad (2)$$

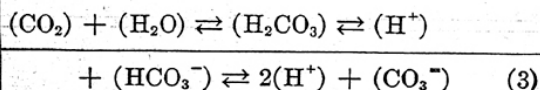
More recent theories describing the gaseous exchange mechanism would alter somewhat the basic elements of the surface film model. The penetration theories of *Higbie* [1935] and *Dankwerts* [1951] discard the stable film approach in favor of random surface replacement, with the exchange constant being proportional to a function of the diffusivity D . Alternatively, *Kishinevski* [1955] has suggested that the exchange constant depends entirely on the intensity of turbulence at the interface and is completely independent of the molecular diffusivity. These theories have been combined in the hybrid concept of *Dobbins* [1964] that assumed a film whose liquid content was subject to continuous replacement. Under conditions of slow film replacement, the *Dobbins* theory approaches the laminar layer model.

The present work provides experimental support for the model of *Lewis* and *Whitman* when used for predicting the surface layer function in carbon dioxide exchange.

CARBON DIOXIDE HYDRATION-DEHYDRATION REACTION

Carbon dioxide exchange across the proposed laminar surface layer is subject to complications arising from the reactions of this gas with water and hydroxyl ions. These reactions, hereafter called hydration-dehydration, may act to produce or remove gaseous CO_2 as it diffuses across the layer. To evaluate the influence of these reactions on the interphase exchange rate, it will be necessary to obtain a general differential equation describing the over-all rate of reaction as a function of pH , known equilibrium constants, and hydration-dehydration rate constants.

Carbon dioxide reacts with water to form carbonic acid, a weak acid that dissociates to produce bicarbonate and carbonate ions. The relative concentrations of the molecular and ionic species are dependent on solution pH ; at a pH of less than 4, the concentration of ionic species is negligible.

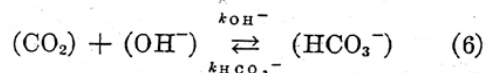
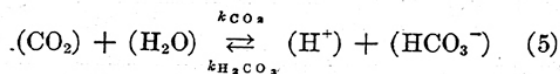


Since the concentration of H_2CO_3 is normally three orders of magnitude smaller than the concentration of dissolved CO_2 [*Bolin*, 1960], the equilibrium between molecular and ionic species is frequently written in terms of the concentration of molecular CO_2 . Equilibrium constants for the reactions given by (3) will therefore be defined by

$$K_1 = \frac{a_{\text{H}^+}(\text{HCO}_3^-)}{(\text{CO}_2)a_{\text{H}_2\text{O}}} \quad K_2 = \frac{a_{\text{H}^+}(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} \quad (4)$$

where a_{H^+} is the hydrogen ion activity as measured by the glass electrode, $a_{\text{H}_2\text{O}}$ is the activity of water (taken to be 1.0 for ionic strength regions employed), and i is the molar concentration of species i .

The reactions of CO_2 with water and hydroxyl ions are governed by rate constants defined according to the equations that follow. To simplify the calculations, the intermediate carbonic acid form will not be shown. The difference between the activity and concentration of the hydrogen ion will not be distinguished in the ensuing mathematical analysis in order to allow simplicity of notation.



These reactions may be summarized by the rate equilibria

$$\frac{k_{\text{CO}_2}}{k_{\text{H}_2\text{CO}_3}} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{CO}_2)(\text{H}_2\text{O})} \quad (7)$$

$$\frac{k_{\text{OH}^-}}{k_{\text{HCO}_3^-}} = \frac{(\text{HCO}_3^-)}{(\text{CO}_2)(\text{OH}^-)} \quad (8)$$

By using the rate definitions of (5) through (8), the hydration and dehydration phenomena may be described formally by an equation for net CO_2 concentration change.

$$\begin{aligned} \partial(\text{CO}_2)/\partial t = & -[k_{\text{CO}_2} + k_{\text{OH}^-}(\text{OH}^-)](\text{CO}_2) \\ & + [k_{\text{H}_2\text{CO}_3}(\text{H}^+) + k_{\text{HCO}_3^-}](\text{HCO}_3^-) \end{aligned} \quad (9)$$

This is the required differential equation describing carbon dioxide hydration and dehydration. However, certain algebraic simplifications will make its application to the surface layer diffusion model considerably more convenient. The

combined rate terms describing hydration may be designated by $\langle k \rangle$

$$k_{\text{CO}_2} + k_{\text{OH}^-}(\text{OH}^-) = \langle k \rangle \quad (10)$$

and the combined rate terms describing dehydration may be replaced by

$$[k_{\text{H}_2\text{CO}_3}(\text{H}^+) + k_{\text{HCO}_3^-}] = \frac{\langle k \rangle (\text{H}^+)}{K_1} \quad (11)$$

This simplification of the dehydration expression assumes $a_{\text{H}_2\text{O}}$ to be unity and may be obtained from (4), (7), and (8). It is now possible to rewrite (9).

$$\frac{\partial(\text{CO}_2)}{\partial t} = -\langle k \rangle (\text{CO}_2) + \frac{\langle k \rangle (\text{H}^+)}{K_1} (\text{HCO}_3^-) \quad (12)$$

For convenience in applying this reaction expression to the surface layer model, it will be necessary to replace the bicarbonate concentration term by an expression that includes the sum of all the CO_2 related species in solution, hereafter called the total CO_2 .

$$\begin{aligned} \sum \text{CO}_2 &= (\text{CO}_2) + (\text{H}_2\text{CO}_3) \\ &\quad + (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \end{aligned} \quad (13)$$

By neglecting the small carbonic acid contribution, this relation may be rewritten as

$$\begin{aligned} \sum \text{CO}_2 - (\text{CO}_2) &= (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \\ &= (\text{HCO}_3^-) \frac{(\text{H}^+) + K_2}{(\text{H}^+)} \end{aligned} \quad (14)$$

which provides the required expression

$$(\text{HCO}_3^-) = \frac{(\text{H}^+)}{(\text{H}^+) + K_2} [\sum \text{CO}_2 - (\text{CO}_2)] \quad (15)$$

This new term involving total CO_2 may be inserted into (12).

$$\begin{aligned} \partial(\text{CO}_2)/\partial t &= -\langle k \rangle (\text{CO}_2) + \frac{\langle k \rangle (\text{H}^+)}{K_1} \\ &\quad \cdot \left[\frac{(\text{H}^+)}{K_2 + (\text{H}^+)} [\sum \text{CO}_2 - (\text{CO}_2)] \right] \end{aligned} \quad (16)$$

Having now obtained the hydration-dehydration expression in a form applicable to the surface layer model, we will find it useful to simplify (16) by defining a new symbol τ .

$$\frac{(\text{H}^+)^2}{K_1 K_2 + K_1 (\text{H}^+)} = \tau - 1 \quad (17)$$

The introduction of the symbol τ makes it possible to write the differential equation for CO_2 hydration-dehydration in the fewest possible terms.

$$\begin{aligned} \partial(\text{CO}_2)/\partial t &= -\langle k \rangle \tau (\text{CO}_2) \\ &\quad + \langle k \rangle (\tau - 1) \sum \text{CO}_2 \end{aligned} \quad (18)$$

This is the form in which the hydration-dehydration expression will be applied to the surface layer model. The rate and equilibrium constants necessary for the determination of $\langle k \rangle$ and τ as functions of temperature, ionic strength, and $p\text{H}$ were obtained from *Harned and Bonner* [1945] and *Pinsent et al.* [1956].

EFFECTS OF CO_2 HYDRATION-DEHYDRATION ON SURFACE LAYER EXCHANGE MODEL

Bolin [1960] has proposed that the rate of CO_2 exchange across an aqueous surface layer would be affected by the hydration-dehydration reactions of this gas with water and hydroxyl ions inside the layer. This would imply that the surface structure of a solution and the CO_2 exchange mechanism are uniquely related and may be studied simultaneously.

A qualitative picture of this relationship may be described easily enough. The concentrations of dissolved CO_2 and the various carbonate species may be assumed to be in thermodynamic equilibrium in the turbulent body of the solution with the relative concentrations being governed by the $p\text{H}$ and temperature. However, the molecular CO_2 concentration gradient across the aqueous surface layer, which results from a net CO_2 sink or source in the gaseous phase, will produce a nonequilibrium CO_2 concentration inside the layer. (It is assumed that the $p\text{H}$ within the layer will be essentially the same as the solution $p\text{H}$, since hydrogen ion mobility is approximately 8 times that of the bicarbonate ion. In addition, the $p\text{H}$ in most natural waters will be stabilized by the buffering action of various weak acid salts.) The molecular and ionic species in the layer will respond to this nonequilibrium CO_2 concentration by a predominance of the hydration or dehydration reaction in the direction that would restore the concentration equilibrium appropri-

ate to the pH. The result of this hydration or dehydration reaction predominance will be the addition or removal of molecular CO_2 by the bicarbonate-carbonate system within the surface layer. As a result of this steady-state non-equilibrium condition, an ionic species gradient will develop and carbon dioxide exchange across the aqueous surface layer will be augmented by the participation of bicarbonate and carbonate ions in the diffusion process. If the aqueous solution is sufficiently basic and the surface layer thick enough, this reaction can significantly increase the exchange over that caused by the simple molecular CO_2 gradient. The use of this phenomenon to selectively increase CO_2 diffusion over that of oxygen through an immobilized film of aqueous bicarbonate-carbonate solution has been reported by *Ward and Robb* [1967].

CALCULATION OF THE IONIC SPECIES CONTRIBUTION TO CARBON DIOXIDE EXCHANGE ACROSS A STAGNANT SURFACE LAYER

Using the laminar layer diffusion model given in (1) and (2), simple gaseous exchange between phases may be described by the following relationship:

$$dq/dt = AD[(C_1 - C_2)/\delta] \quad (19)$$

with terms previously defined. In this model, the linear gaseous concentration gradient is simply the concentration difference between the upper and lower edges of the layer divided by the layer thickness. However, to represent the contribution to exchange resulting from a net bicarbonate- CO_2 interconversion and the coincident bicarbonate gradient in the layer, an additional factor must be included in the simple gaseous gradient model to represent the increased exchange. This is most conveniently done by introducing the term m to represent the total CO_2 gradient and relating this term to the simple gaseous gradient by the factor α .

$$m = \alpha[(C_1 - C_2)/\delta] \quad (20)$$

The following development, in which the term α is derived, was first advanced by *Bolin* [1960]. More recently, the same treatment was developed independently (*R. F. Miller*, personal communication, 1963) in a somewhat simpler form owing to the use of hyperbolic identities,

and the derivation presented here will utilize this simplified approach.

The gaseous and the total CO_2 diffusion equations will be subject to four boundary conditions. For the equations, one-dimensional diffusion will be allowed along an axis designated as y . For this model, $y = 0$ at the phase interface and $y = \delta$ at the lower side of the stable surface layer. The concentration of carbon dioxide at the lower side of the layer ($y = \delta$) will be defined as

$$(\text{CO}_2) = C_L \quad \text{at } y = \delta \quad (21)$$

where C_L is the concentration of CO_2 in the body of the solution.

The concentration of CO_2 at the phase interface ($y = 0$) will be defined as

$$(\text{CO}_2) = \psi C_g \quad \text{at } y = 0 \quad (22)$$

where C_g is the concentration of CO_2 in the gaseous phase and ψ is the solubility constant of carbon dioxide in water.

The molecular and ionic carbon dioxide species are assumed to be in the ratio required for equilibrium at the pH existing at the lower boundary of the layer ($y = \delta$).

$$C_L = \sum \text{CO}_2 [(\text{CO}_2) / \sum \text{CO}_2]_{\text{equilibrium}} \quad \text{at } y = \delta \quad (23)$$

The fourth condition will be to allow only gaseous diffusion into the gas phase; no ionic forms are allowed into the gas phase. Therefore, at $y = 0$

$$\partial \sum \frac{\text{CO}_2}{\partial y} = \frac{\partial(\text{CO}_2)}{\partial y} \quad \text{at } y = 0 \quad (24)$$

These four boundary conditions will be applied to the two differential equations for total CO_2 and molecular CO_2 exchange across a laminar surface layer. These equations follow from the classical flux definitions. The total CO_2 diffusion must be defined as

$$\begin{aligned} [\partial \sum \text{CO}_2 / \partial t]_v &= D_{\text{CO}_2} [\partial^2(\text{CO}_2) / \partial y^2] \\ &+ D_{\text{HCO}_3^-} [\partial^2(\text{HCO}_3^-) / \partial y^2] \\ &+ D_{\text{CO}_3^{2-}} [\partial^2(\text{CO}_3^{2-}) / \partial y^2] \end{aligned} \quad (25)$$

where D is the diffusivity. Since the diffusivity reported for ionic species resembling carbonate and bicarbonate is approximately the same as

the diffusivity of molecular CO₂, it is possible to consider their diffusivity analogous to that of the molecular species and to simplify (25) to a more convenient form.

The total CO₂ diffusion is accordingly

$$[\partial \sum \text{CO}_2 / \partial t]_v = D_{\text{CO}_2} [\partial^2 \sum \text{CO}_2 / \partial y^2] \quad (26)$$

In like manner, the molecular diffusion is described by

$$[\partial(\text{CO}_2) / \partial t]_v = D_{\text{CO}_2} [\partial^2(\text{CO}_2) / \partial y^2] + H \quad (27)$$

The term H in this expression represents the rate of creation or depletion of molecular CO₂ in the surface membrane by hydration and dehydration, given in (18). Since there is no detectable alteration in the gradient over a limited time period, the time derivatives may be set to zero. This makes it possible to write (26) and (27) as

$$D[\partial^2 \sum \text{CO}_2 / \partial y^2] = 0 \quad (28)$$

and

$$D[\partial^2(\text{CO}_2) / \partial y^2] = -H \quad (29)$$

The solution to (28) may be written by inspection

$$\sum \text{CO}_2 = my + b \quad (30)$$

and the total carbon dioxide gradient is therefore m .

Equation 29 may be rewritten using the expression for hydration-dehydration given in (18), with a substitution for the total CO₂ being made from (30).

$$\begin{aligned} \partial^2(\text{CO}_2) / \partial y^2 \\ = \frac{\langle k \rangle \tau}{D} (\text{CO}_2) - \frac{\langle k \rangle (\tau - 1)}{D} (my + b) \end{aligned} \quad (31)$$

This may be solved for CO₂ concentration as a function of location in the layer

$$\begin{aligned} (\text{CO}_2) = A \cosh \left[\left(\frac{\langle k \rangle \tau}{D} \right)^{1/2} y \right] \\ + B \sinh \left[- \left(\frac{\langle k \rangle \tau}{D} \right)^{1/2} y \right] \\ + \left[\frac{\tau - 1}{\tau} \right] (my + b) \end{aligned} \quad (32)$$

A judicious substitution of the boundary conditions will eliminate the integration constants A , B , and b and will permit a solution for the total CO₂ gradient m in terms of known parameters

$$m = \frac{(C_L - \psi C_s)}{\delta} \alpha \quad (33)$$

where

$$\alpha = \frac{\tau}{(\tau - 1) + \left\{ \tanh \left[\left(\frac{\langle k \rangle \tau}{D} \right)^{1/2} \delta \right] / \left(\frac{\langle k \rangle \tau}{D} \right)^{1/2} \delta \right\}} \quad (34)$$

The total CO₂ gradient is therefore a product of the gaseous concentration gradient and α , a complex expression that includes the layer thickness δ , the pH (which determines τ), the rate of CO₂ hydration, and the molecular diffusivity D . For this work, calculated values of the term α were compared against the values measured experimentally.

APPARATUS AND DATA COLLECTION

The experimental procedure was designed to monitor the rate of gaseous diffusion from a body of water in a simulated natural environment and employed a thermally regulated 230 × 30 × 25-cm water tank in a variable speed wind tunnel. The wind was allowed to flow smoothly along the entire length of the tank, and mechanical arrangements made it possible to vary the wind speed from 1.0 to 7.0 m/sec. The 180-liter tank was filled with a distilled water solution of sodium citrate buffer and the level was maintained to ±1.0 mm. For the low pH experiments 0.36 mole of citric acid were used, producing a citrate concentration of 0.002 mole/liter and a pH of approximately 3.0. In the high pH experiments 0.36 mole of sodium citrate was added to the tank and the pH was adjusted down to about 6.5 with HCl. Citrate was the only usable buffer in this pH range, and it was used in both high and low pH experiments to maintain ionic strength continuity. The first dissociation constant of carbonic acid is dependent on temperature and ionic strength, and it was calculated specifically for each experiment from the thermodynamic dissociation constant, using activity coefficient data published by *Harned and*

Bonner [1945]. The temperature of the water tank was maintained constant to $\pm 0.1^\circ\text{C}$ by means of thermostatically controlled coolant flow in glass coils situated along the interior walls of the tank. The $p\text{H}$ was determined to ± 0.01 unit with a Beckman Zeromatic $p\text{H}$ meter, and there was no measurable $p\text{H}$ shift in the solution during the periods of experimentation. The water tank was fashioned from thick plywood and the interior heavily coated with a chemically resistant paint.

To simulate natural turbulence in the body of the liquid, a small external pump was utilized to withdraw water at the surface near one end of the tank and to return it at the bottom near the opposite end. A volume of water equal to that of the tank was circulated by the pump every 45 min. It was found that modest fluctuations in the rate of pumping did not influence the carbon 14 depletion process. This pumping arrangement provided the necessary temperature and solute homogeneity in the body of the solution without disturbing any surface layering which might be present. The temperature of the tank was continuously monitored at various heights to detect any possible temperature gradients, and checks were made to validate the assumption that no concentration gradients of the carbon 14 species existed in the body of the solution. It was found that the artificial turbulence provided by the pump was necessary and sufficient to prevent temperature and concentration gradients. The air speed was monitored intermittently with a fan type anemometer, and all wind speeds were completely reproducible during the period of experimentation. The temperature of the solution was maintained in a region above the atmospheric dew point, since preliminary indications were that condensation on the surface of the water could effectively stop gaseous exchange.

The rate of CO_2 exchange between the two phases was measured by using a carbon 14 tracer. A small amount of carbon 14 in the form of dissolved carbonate was added to the solution in a concentration sufficient for rapid counting techniques, and samples were periodically withdrawn for analysis. The carbonate tracer, of course, immediately assumed the molecular-ionic equilibrium appropriate to the solution $p\text{H}$. The airstream was taken from and ducted directly back into the out-of-doors, and the

inflowing air was considered to have a zero concentration of C^{14}O_2 at all times. The rate of carbon 14 depletion was unaffected by the net uptake or release of nonradioactive CO_2 in the tank, since the carbon 14 tracer constituted an independent molecular species. It was assumed that there was no appreciable isotopic fractionation in the diffusion process.

Triplicate 10-ml solution samples were withdrawn periodically from the geometric middle of one side of the tank, added to a flask containing a carbonate carrier, and precipitated with $\text{Ba}(\text{OH})_2$. They were then analyzed for their total carbon 14 content by counting the filtered precipitate in a Nuclear-Chicago gas flow beta detector. The experimental routine provided paired low $p\text{H}$ and high $p\text{H}$ carbon 14 depletion slopes over a variety of air speeds (i.e. surface layer thicknesses). By obtaining the depletion slopes for a given air speed under two separate $p\text{H}$ conditions, it was possible to determine values for the two unknown parameters: (1) the surface layer thickness δ and (2) the exchange acceleration α_0 at high $p\text{H}$ caused by the ionic gradient. These two parameters may be extracted from the total carbon 14 depletion slope using the following relationship, which can be derived from the diffusion equations:

$$\text{Slope} = \frac{1}{d} \cdot \frac{D}{\delta} \cdot \alpha_0 \cdot \frac{\tau - 1}{\tau} \quad (35)$$

where d is the depth of the tank. The term including τ converts total carbon 14 depletion to C^{14}O_2 depletion. This data analysis makes it possible to evaluate simultaneously the theory of a laminar surface layer as well as the role of this layer in CO_2 exchange.

EXPERIMENTAL RESULTS VERSUS STAGNANT LAYER MODEL PREDICTIONS

Twenty-three carbon 14 depletion experiments are reported in Table 1. The low $p\text{H}$ experiments were all executed in a $p\text{H}$ region below 4, at which carbon dioxide occurs almost entirely in the molecular form and acts effectively as an inert gas. The high $p\text{H}$ experiments employed a solution $p\text{H}$ near 6.5 (values ranged from 6.375 to 6.742). In this $p\text{H}$ region, a significant portion of the carbon 14 was in the form of anions. The C^{14}O_2 exchange constant was significantly higher at the higher $p\text{H}$ region,

TABLE 1. Carbon Dioxide Exchange at Low pH (<4.0) and High pH (6.375 < pH < 6.742) with Comparison of Observed versus Predicted Exchange Increase at High pH

Air Speed, m/sec	Water Temp., °C	Calculated Surface Layer Thickness δ , mm	Low pH Exchange Constant k , cm/hr	High pH Exchange Constant k , cm/hr	Observed High pH Exchange Increase, α_0	Predicted High pH Exchange Increase, α	Predicted versus Observed, % Difference
1.5	20	0.615	0.88	1.53	1.73	1.76	1.7
1.5	20	0.610	0.89	1.42	1.60	1.66	3.8
3.1	20	0.257	2.11				
3.7	20	0.223	2.44				
4.2	20	0.198	2.75				
5.1	20	0.161	3.37				
5.4	20	0.150	3.62				
1.0	25	0.547	1.10				
1.5	25	0.548	1.10	2.05	1.87	1.73	7.5
1.5	25	0.539	1.12	1.88	1.68	1.68	0.0
3.0	25	0.295	2.04	2.86	1.40	1.30	7.0
3.7	25	0.224	2.68	3.23	1.23	1.20	2.4
4.2	25	0.181	3.31	3.72	1.12	1.14	1.8
4.6	25	0.146	4.14	4.72	1.14	1.10	3.5
7.0	25	0.056	10.80				

indicating an ionic gradient contribution to the exchange and, coincidentally, supporting the

validity of the laminar layer model. Certain low pH exchange constants reported in Table 1 lack a corresponding high pH experiment; they are included solely as a further illustration of the relationship between air speed, temperature, and surface layer thickness.

The thickness of the surface layer is inversely related to the wind speed, and values for this parameter were obtained from the low pH exchange constant using the relationship given in (2). The exchange enhancement due to the bicarbonate interconversion is dependent on layer thickness, and it can be seen from Figure 1 that for the pH region around 6.5 no significant effect was observed at air speeds above 5 m/sec.

The layer thickness is assumed to be identical for high and low pH measurements at a single wind speed. Since the exchange enhancement factor is 1.0 at low pH conditions, the experimentally observed high pH exchange enhancement may be obtained by a simple division of the two rate constants.

$$\frac{\text{EXPERIMENTAL EXCHANGE}}{\text{ENHANCEMENT FACTOR}}$$

$$= \alpha_0 = \frac{k_{\text{high pH}}}{k_{\text{low pH}}} \quad (36)$$

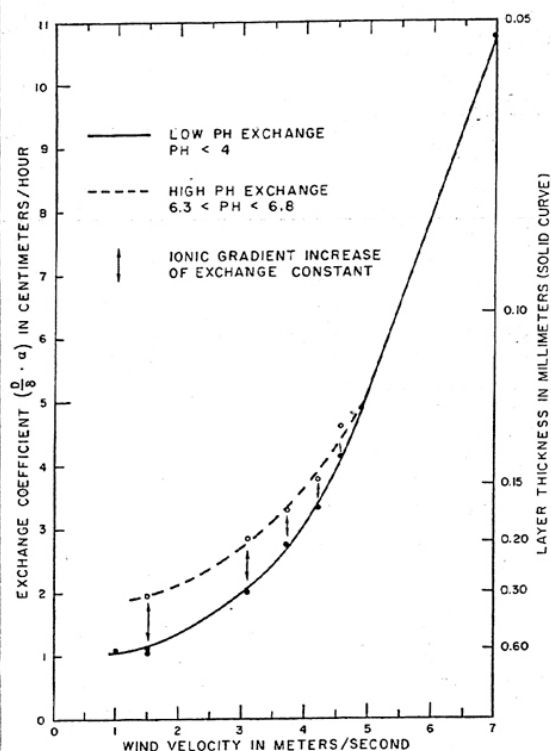


Fig. 1. Carbon dioxide exchange coefficient at low pH and high pH shown as a function of air speed.

Experimentally obtained values for α_0 are given in Table 1.

If the laminar layer model is an accurate representation of the exchange process, the experimental exchange enhancement factor α_0 could be expected to correspond to the theoretical exchange enhancement factor α given in (34). Values for the theoretical exchange enhancement factor α were computed using the layer thickness and pH conditions associated with each high pH experiment. A tabulation of α is given in Table 1 alongside the observed α_0 and their correspondence is related by per cent difference. Within the limits of experimental error, the stagnant layer model appears to provide satisfactory predictions, and the layer concept would seem to be a profitable method of describing exchange in this particular environment.

Although few models have been subjected to the rigorous test given the Lewis-Whitman model here, it is possible that other theoretical constructions may provide comparable pH predictions. Certainly further research is needed to elucidate fully the mechanics of gaseous interphase exchange. Theoretical justification notwithstanding, these experiments firmly support the sometime contested proposition that carbon dioxide interphase exchange is influenced by solution pH and that the extent of this influence is a function of the relative motion between the phases; the anticipation of the precise extent of this effect by the two-layer model only embellishes the observations. It should be added that this demonstration of the influence of hydration on CO₂ exchange indicates a greater effect than was reported by Kanwisher [1963], whose work closely parallels that presented here.

POSSIBLE EFFECTS ON OCEANIC CARBON DIOXIDE EXCHANGE

Over the past few years there has been heightened interest in the rate of CO₂ exchange between the atmosphere and the sea. By using the development presented here in conjunction with the appropriate sea water constants, it is possible to provide a sample calculation of the potential effects of the CO₂ reactions on sea water exchange. The examples shown in Table 2 purposely employ low wind speed conditions where the effects of CO₂ reactivity on exchange have been seen to be the most pronounced.

TABLE 2. Potential Increase in CO₂ Exchange Rate across Ocean's Surface at 19‰ Chlorinity and 20°C Temperature

Surface Layer Thickness, mm	(Corresponding Air Speed in Tunnel), m/sec	Oceanic pH	Carbon Dioxide Exchange Enhancement, α
0.3	3.0	7.0	1.62
0.3	3.0	8.0	1.62
0.3	3.0	9.0	1.66
0.6	1.3	7.0	2.65
0.6	1.3	8.0	2.67
0.6	1.3	9.0	3.04

Although the wind tunnel results certainly should not be extrapolated without qualification to the ocean, a critical comparison is instructive. Average 'layer thicknesses' deduced from studies of worldwide radiocarbon distribution support the intuitive judgment that the average open ocean is far too turbulent to allow the sort of surface layer thicknesses observed in the experimental tank. However, the possibility that hydration may influence CO₂ exchange in sheltered, placid regions should not be dismissed out of hand. In particular, localized studies of CO₂ exchange (such as diurnal studies in coves) that are accompanied by quiescent wind conditions may be sensible to this effect. In the last analysis, however, resolution of the many complexities of the worldwide CO₂ system must await more direct exchange measurements on the open ocean.

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