JOURNAL OF MARINE RESEARCH

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Mass Transfer of Carbon Dioxide
Across Sea Surfaces

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ABSTRACT

The rate of mass transfer of carbon dioxide across the sea surface was investigated in the laboratory and at sea. In the laboratory, radioactive tracer techniques were employed using high specific activity $C^{14}O_2$. The equilibrium distribution of CO_2 is not affected greatly and the mass transfer measured is very nearly the exchange coefficient. The mass transfer at sea was measured in a closed system using a recirculated sample stream from the gas phase and a nondestructive infrared analyzer. The data indicate that the rate of transfer is controlled by turbulent processes in the water phase and that the reaction is of first order. It was not possible to eliminate turbulence in the air phase, and the data may reflect the fact that the effective mixing time in the air phase was short compared to the time of sampling; that is, small differences in the air phase do not last long enough to be detected in either analytical system. Results indicate that the transfer of CO_2 from the atmosphere to the sea may not be the limiting factor controlling the residence time of CO_2 in the atmosphere. The experiments are of a preliminary nature and are not offered as final conclusions.

Introduction. The CO_2 exchange between atmosphere and ocean has recently received wide attention (Callender, 1940; Plass, 1956; Revelle and Suess, 1957) because of possible increased atmospheric content from burning fossil fuels. Craig (1957) and Bolin and Eriksson (1959), using bomb-produced C^{14} as the indicator, have calculated a residence time for CO_2 in the atmosphere of 5 to 6 years. An oceanic exchange rate of 1.77×10^{-4} mg/cm²/min would be required to provide a residence time of 7 years. It is obvious that there must be considerable variations in the exchange rates in different regions of the ocean and in the same regions under different environmental conditions. Attempts to measure the invasion coefficient (α) for sea water in different laboratories have produced a wide range of values depending on experimental conditions. Values of 0.033 and 6.6 mg/cm²/atm/min for a static film (Becker, 1924) and for a vigorously agitated solution (Guyer and Tobler, 1934) respectively have been reported.

According to Lewis and Whitman's two-film theory of gas transfer between reservoirs (Hutchinson, 1957), nonturbulent films are formed on each

side of the interface – by the gas on the atmospheric side and by water on the liquid side. In dealing with CO_2, a very soluble minor constituent, the rate of entry of gas molecules into each film must be considered, this being by the rate of surface removal, which is dependent upon turbulence. Since turbulent diffusivity in the sea is known to be as much as 10^6 times greater than molecular diffusivity, it is expected that the water surface film will be rapidly renewed under most sea conditions. Turbulence of the air above the sea is also great in comparison to molecular diffusion. Thus, the transfer of CO_2 across the water-air interface is dependent upon the turbulence of the medium on either side of the interface, rather than through diffusion in either phase. It is possible that the rate of transfer is controlled by either, or both, of the two surface films. If only one film is controlling, then it would be expected that the forward and the backward rate constant (k_f and k_b respectively) would be defined by a first order reaction; however, if both films are involved, a deviation from the first order would be expected. This study was undertaken to elucidate the mechanism of transfer and also to evaluate the invasion coefficient for CO_2 under both laboratory and field conditions.

Theoretical. The rate of transfer in the local environment bears a significant relation to the dynamics of all biogeochemical processes associated with the carbonate-carbon dioxide system. Evaluation of this factor requires direct measurement of mass transfer rates of CO_2 through the sea surface.

The invasion coefficient of a slightly soluble gas from the gas-phase into the liquid-phase was defined by Bohr (1899) as α in the expression

$$\frac{dQ}{dt} = -\alpha \, A \Delta P , \qquad (1)$$

where dQ/dt = mg of gas/min, A = the surface area in cm², $\Delta P = P_{(g,g)} - P_{(g,aq)}$ in atm at time t, and α = the invasion coefficient in mg/cm²/min/atm.

This equation applies in a given set of conditions with small values of ΔP. However, if the process is limited by diffusion or by rate of replacement of surface film, a unique value of α will be found for each value of these parameters. Field experiments were undertaken to measure α graphically and to test the influence of diffusion and surface film replacement.

The chemical equation for the process,

$$CO_2 \, (g,g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO_2 \, (aq, g), \qquad (2)$$
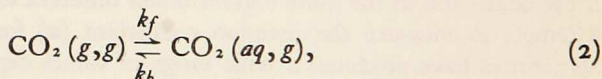
indicates that there are two rate constants, k_f and k_b for the forward and backward reactions respectively. While time is not a factor in the equilibrium constant, information regarding mass transfer is gained by investigating the individual rate constants at various conditions of turbulence both in the gas

and aqueous phase. The influence of temperature and salinity on the transfer will also aid in evaluating the limiting values for the invasion coefficient.

By introducing minute amounts of radiocarbon dioxide tracer to the gas phase over sea water at equilibrium with air and by allowing the reaction to proceed without interference, the concentration of radiocarbon in the liquid phase will increase steadily with time to a maximum value. The rate at which activity decreases in the gas phase must be equal and opposite to the rate at which the $C^{14}O_2$ content of the water phase increases.

If the reaction (eq. 2) proceeds without interference from interface hold-up or limitation by diffusion or hydration processes, it is possible to write the general differential equation representing the kinetics of the transfer:

$$\frac{d N_{gt}}{dt} = - k_f N_{gt} + k_b F N_{lt}, \tag{3}$$

where $N_{gt} = CO_2$ concentration in moles/liter in the gas phase at time t, F = the free CO_2 fraction in the water phase, and N_{lt} = total CO_2 in moles/l in the water phase.

Since $N_{lt} V_l = (N_{go} - N_{gt}) V_g$ (4), we may substitute for N_{lt} in (3) and integrate, giving

$$N_{gt} = \frac{k_b F V_g}{K V_l} N_{go} + \frac{k_f}{K} N_{go\,e} - Kt, \tag{5}$$

where $$K = k_f + k_b F (V_g/V_l). \tag{6}$$

Equation (1) may be transformed into the same form as (3) by substituting for ΔP the term

$$\Delta P = N_{gt} RT - F N_{lt} S, \tag{7}$$

where R = gas constant in l/atm/°K mole, T = temperature in °K, and $S = CO_2$ concentrations in moles/l at saturation under one atm pressure of CO_2 (Harvey, 1957).

Expressing Q in grams,

$$Q = 44 V_g N_{gt}. \tag{8}$$

Equation (1) becomes

$$\frac{d N_{gt}}{dt} = - \left(\frac{A R T}{44 V_g}\right) N + \left(\frac{\alpha A F}{44 V_g S}\right) N_{lt}, \tag{9}$$

which, by comparing (9) and (3)–(5), leads to

$$K = \frac{A}{44 V_g} R T + \frac{V_g F}{V_l S}, \tag{10}$$

$$k_f = \frac{\alpha A R T}{44 V_g}, \tag{11}$$

$$k_b = \frac{\alpha A}{44 V_g S}, \tag{12}$$

$$\alpha = \frac{44 V_g K}{A R T + (V_g F / V_l S)}. \tag{13}$$

Experimental : A. LABORATORY MEASUREMENTS.

1. Apparatus. The apparatus used for the laboratory kinetic studies is shown in Fig. 1. Sea water (300 ml) was placed in the three-necked reaction chamber, the center neck of which was sealed with a mercury glass seal stirrer that served to prevent gas interchange with laboratory air and to regulate pressure. A black and white striped target wheel, attached to the stirrer above the mercury seal, was used as a target for measurement of the stirring rate with a stroboscope. The stirrer speed was altered by means of a variable-speed, 1/30th hp stirring motor and variac. The third neck of the flask was equipped with a rubber stopper carrying two capillary tubes, connected to one of the two arms of the gas burette; one arm was connected to a mercury pump absorption chamber for sampling the gas phase in the reaction chamber, the other to the $C^{14}O_2$ generating system through which the labeled CO_2 was introduced. The gas generator consisted of a closed U-tube to which a side arm was attached at the middle of the U. C^{14}-labeled $BaCO_3$ was placed in
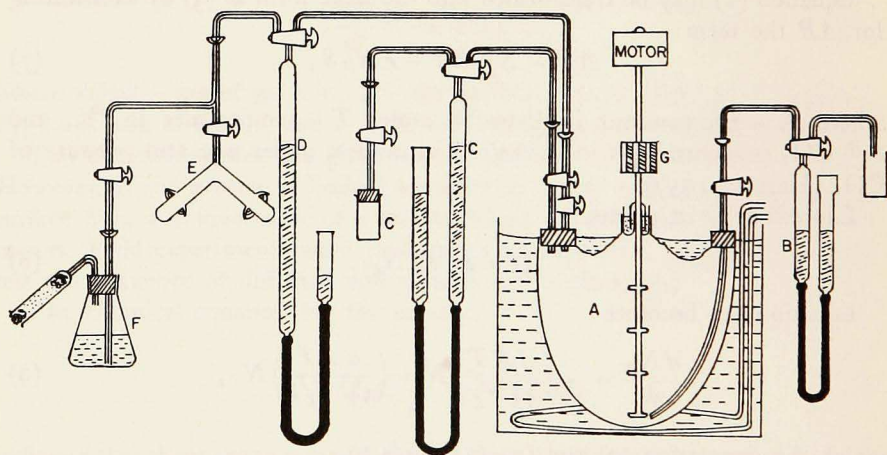

Figure 1. Schematic drawing of the apparatus used for CO_2 transfer studies. A, three-necked reaction flask; B, sea water sampling burette; C, gas sampling burette; D, $C^{14}O_2$ gas measuring burette; E, gas generating chamber; F, source of sodium hydroxide for gas absorption; G, stroboscope target.

one end of the tube and $HClO_4$ in the other. By rotation of the U-tube, CO_2 was generated. The CO_2 absorber containing 100 ml of 2 N NaOH was used for collection of $C^{14}O_2$ at the completion of the experiment.

Temperature control was maintained by means of a Brownwill Temperature Controller and stirrer, bucked by a continuous flow of refrigerated coolant. The sea water sampler was calibrated at 0.5, 1.0, and 2.0 ml, and the gas burette at 5 and 10 ml; the gas collector had graduated intervals from 0.67 ml to 0.5 ml.

2. Radioactivity Measurements. The C^{14} activity of the samples was measured by means of the Packard TriCarb Liquid Scintillation Beta Spectrometer (Packard Instrument Co., Inc., LaGrange, Illinois). To obtain homogeneous distribution of the sample in the scintillating liquid as well as high efficiency of counting, a thixotropic gel system was used. It was found that a maximum count rate was obtained with this system if the samples were allowed to stand at freezer temperature ($-5°$ C) for a period of 15 hours before counting.

3. Reagents. Sea water (18.24 % chlorinity) used in this experiment was collected in the Gulf of Mexico at 25°45′N, 95°10′W. The water was filtered through Whatman No. 1 filter paper and stored at room temperature in a rubber-stoppered Pyrex glass bottle until used. The low chlorinity water used was made by dilution with distilled water.

$BaC^{14}O_3$, to provide $C^{14}O_2$, was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. The specific activity was 0.127 mc/mg. PPO (2,5-diphenyloxazole) was used as a primary fluor, and POPOP (1,4-bis-2)-phenyloxazole (benzene) as a wave shifter.

Toluene fluor solution was made up to contain 25 g of thixotropic gel powder, 4 g of PPO, and 0.1 of POPOP/l of solution.

Experimental: B. Field Experiments.

The field experiments were conducted aboard the R. V. Hidalgo while it was anchored north of Alacran reef in the southern Gulf of Mexico, during February 1960.

1. Apparatus. A schematic drawing of the apparatus used to measure the CO_2 exchange at sea is shown in Fig. 2. The capsule consisted of a 28-inch tractor-tube covered with 1/64-inch sheet neoprene, with an 8-inch weighted neoprene skirt to prevent escape or entrance of gas under wave action. The apparatus did not leak. This was confirmed by comparing the equilibrium partial pressure of CO_2 in the hemisphere and that measured directly by means of infrared analysis of an air stream equilibrated with water pumped from the sea surface. The assemblage was sealed with aluminum foil to help prevent temperature excursions inside the capsule. Tygon tubing attached to the gas chamber with valve stems was used to convey the gas to and from the capsule. The gas in the capsule was sampled continuously by means of a

$C_\dagger = C_{CO_2}$ AT TIME $\dagger$
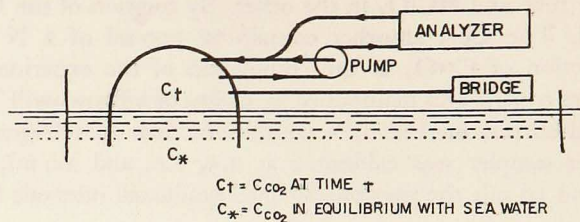$C_* = C_{CO_2}$ IN EQUILIBRIUM WITH SEA WATER

Figure 2. Schematic drawing of apparatus for kinetic study at sea.

vacuum-pressure diaphragm pump, circulating approximately 2 l/min. The total pressure differential was never allowed to exceed three inches of water above atmospheric pressure. A portion of the gas stream was passed through an Applied Physics Infrared Gas Analyzer for continuous analyses. The temperature inside the capsule was measured by a thermistor bridge, with the sensor mounted near the center of the air phase. The area of surface covered by the capsule was calculated to be 3,970 cm², and gas volume was approximately 100 l.

At the beginning of the experiment, CO_2, generated by adding H_2SO_4 to $NaHCO_3$, was pumped into the capsule air volume. After circulating the CO_2 for approximately 20 minutes to provide a homogeneous mixture, analyses of the gas stream were initiated. In the evasion experiment, gas from the capsule was passed over solid KOH for a period of 30 minutes in order to lower the CO_2 tension in the gas phase. The KOH pellets were then by-passed and the rate of increase of CO_2 in the gas phase was measured. The infrared gas analyzer was calibrated against standard gases of known concentrations.

Results and Discussion. Results of laboratory measurements using $C^{14}O_2$ in sea water of 18.24 °/$_{oo}$ chlorinity at 20°C are shown in Fig. 3. It is evident in Fig. 3 that the value of

$$\frac{A_{l_\infty} - A_{lt}}{A_{l_\infty}},$$

where A_{l_∞} = activity C^{14} in liquid phase at $t = \infty$, and A_{lt} = activity of C^{14} in liquid phase at time t, plotted against t for each run at constant stirrer speed, produces a value for K for that set of conditions.

The values of K plotted against stirring speeds are shown in Fig. 4. The curve produced may be expressed by

$$K = 0.420 + 0.894 \times 10^{-3} \cdot \Omega + 1.860 \times 10^{-6} \cdot \Omega^2 + 8.024 \times 10^{-10} \cdot \Omega^3, \quad (14)$$

where K expresses the exchange rate constant per hour and Ω the speed of the stirrer in revolutions/min. The value of K extrapolated to zero stirring
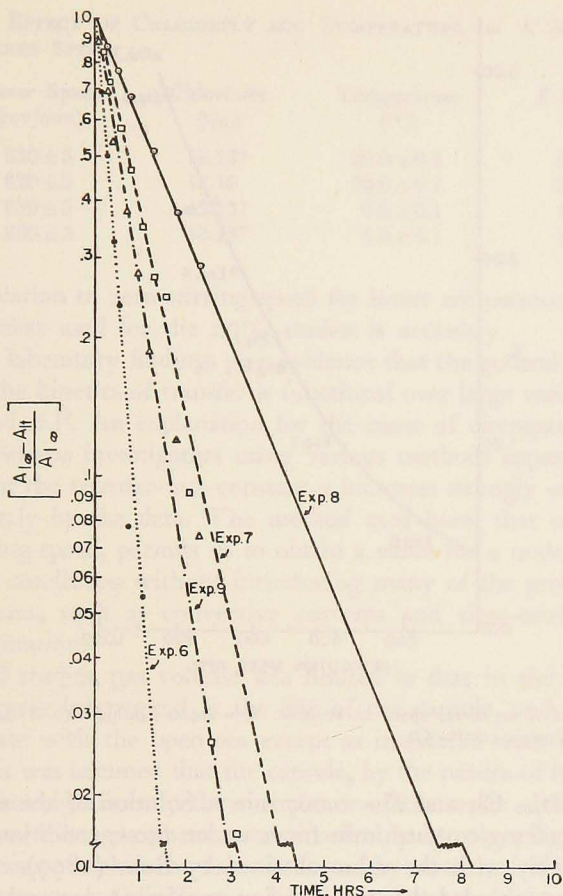
Figure 3. Semilog plot of $Al_\infty - Al_{lt})/Al_\infty$ vs t for measurement of K CO_2 under simulated sea surface conditions.

speed, or the exchange rate constant under undisturbed film conditions over a homogeneous water, is estimated to be 0.420 per hour.

The effects of chlorinity and temperature on the value for K, associated with a given speed, are shown in Table 1.

The relationship between chlorinity, temperature, and K-value was determined at 830 revolutions/min of the stirrer. From these data it is seen that the exchange rate constant does not change with chlorinity over 12–18%, but decreases with decreasing temperature.

Substitution in (13) will yield the invasion coefficient α for the transfer of CO_2 through the simulated sea surface at zero stirring speed. $A = 190$ cm², $V_g = 5.16$ l; $V_l = 0.300$; $f = 0.005$ (pH 8.3 and 20°C); $s = 0.0343$ moles/l
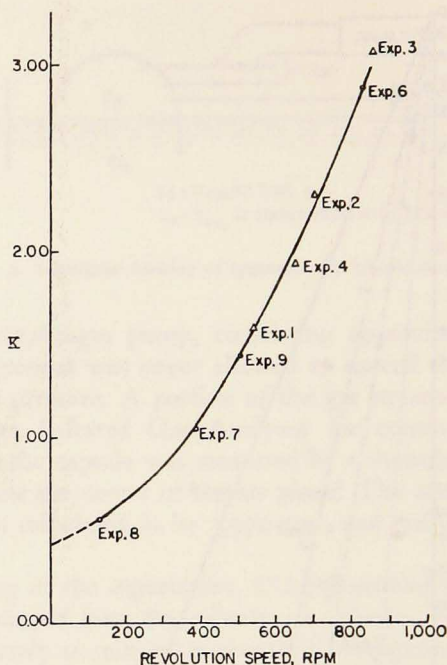
Figure 4. Plot of K vs stirrer speed in rev/min. $K = 0.420 + 0.894 \times 10^{-3} \cdot \Omega + 1.860 \times 10^{-6} \cdot \Omega^2 + 8.024 \times 10^{-10} \cdot \Omega^3$.

at 20°C and 18⁰/₀₀ Cl; and $K = 0.007$ min⁻¹. Solution of the equation gives a value of 0.316 mg/cm²/atm/min for α under these conditions; this value compares favorably with the value obtained by Bohr (1899).

It cannot be concluded that the invasion coefficient decreases as rapidly as K, since from (13), by arbitrarily setting the experimental parameters V_l and V_g equal to 44, (13) then takes the form

$$\alpha = \frac{K}{RT + \dfrac{F}{S}}. \qquad (15)$$

Substituting for T, F, and S, as given by Harvey, at 0° and 20°C, we find

$$\alpha = K\,(0.0445) \text{ at } T = 0°C \text{ and}$$
$$\alpha = K\,(0.0414) \text{ at } T = 20°C.$$

It is seen from this example that the value of $1/(RT + F/S)$ in (15) increases with decreasing temperature. To obtain the correct relation of α to temper-

TABLE I. EFFECT OF CHLORINITY AND TEMPERATURE ON K ASSOCIATED WITH STIRRER SPEED.

Stirrer Speed (rev/min)	Chlorinity ($^o/oo$)	Temperature (°C)	K hour^{-1}
830 ± 5	18.237	20.0 ± 0.1	2.88
830 ± 5	12.16	20.0 ± 0.1	2.88
830 ± 5	18.237	6.0 ± 0.1	1.54
800 ± 5	18.237	6.0 ± 0.1	1.44

ature, extrapolation to zero stirring-speed for lower temperatures by the same procedure as that used for the 20°C studies is necessary.

The above laboratory findings give evidence that the general Bohr equation representing the kinetics of transfer is functional over large variations in water turbulence and ΔP. An explanation for the cause of discrepancy in α values obtained by various investigators using various methods appears to be found in the fact that the transfer-rate constant α increases strongly with turbulence, as shown clearly by the data. The method used here, that of extrapolating the zero stirring speed, permits us to obtain a value for α under nonturbulent homogeneous conditions without introducing many of the problems inherent in static systems, such as convective currents and time-established surface molecule orientation.

In the field studies, gas volume was limited to that in the closed capsule, water surface was interrupted at the site of the capsule, and the water was free to circulate with the open sea except as interfered with by the capsule. In this work it was assumed that the capsule, by the nature of its construction, would not affect significantly the turbulence of the water either at or below the sea surface. The gas phase was stirred only by pumping and by slight changes in pressure within the capsule caused by wave and wind action. It is realized that these conditions are unlike normal sea conditions. However, a choice had to be made — to allow the normal turbulent motion of the sea to exist and limit the air motion, or to limit the turbulence of the water and permit the air to circulate as might be done by use of a wind tunnel. The use of a wind tunnel on the sea surface may be possible, but this did not lend itself to immediate solution as part of these experiments. Our choice of confining the gas phase in these studies was predicated by consideration of the physics of the problem as discussed by Bolin (1961) and by consideration of the much higher mean free path of the gas molecule in the gas phase as compared to the water phase. These considerations lead one to believe that the transfer of a gas would be controlled primarily by turbulence of the water rather than by the turbulence of the air. Turbulence of the water arises primarily from wind stress, secondarily from evaporation and radiactive cooling of the surface waters; however, these effects are realized over large areas of the ocean and are not thought to be minimized by the techniques
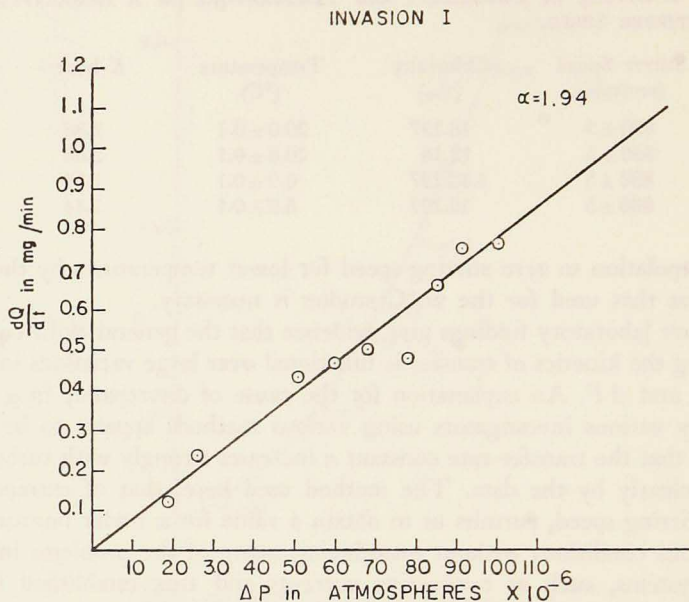
INVASION I

Figure 5. Plot of dQ/dt vs. ΔP for invasion of CO_2 into sea water oΔ. Location: 89°49'W, 22° 33'N, 2 miles SW of north lighthouse on Alacran Reef, Gulf of Mexico. Depth: 10 fathoms; time: 1400 local; weather: clear, windspeed 15 knots, wind direction NE; sea surface: 2–3' waves, occasional caps; sea surface temperature: 22.4°C; free air temperature: 23.6°C; capsule temperature: 23.8°C; chlorinity: 20.2°/₀₀.

used in this experiment even though the local air movement is substantially changed.

The results of experimental runs (Figs. 5, 6) indicate a first order reaction. The plot of dQ/dt versus ΔP (1) produces a straight line, the slope of which is αA. The value of α was calculated. The observed values for α in the two invasion experiments at a single station, under conditions that vary significantly only in the time of day and in the turbulence of the water, show a marked change in mass transfer rates of carbon dioxide.

The values for α and K obtained in this study and in those reported previously by Bohr (1899), Becker (1924), Y. Miyake and A. Hamada (personal communication), and Guyer and Tobler (1934) are presented in Table II. The third column in Table II represents α calculated on the piston concept of invasion by converting mg/cm²/atm/min to cm/min. This then measures the rate at which a column of pure CO_2, under a pressure of one atmosphere, would move through the sea surface. The values fall into three categories: the slow rate in a static system, as determined by Becker and by Miyake and Hamada; the intermediate rate in a system under mild agitation, as determined
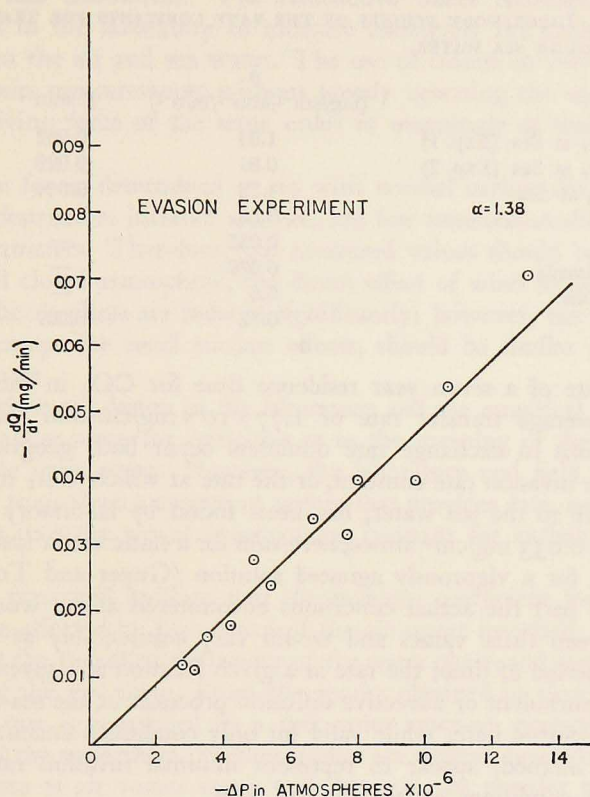
Figure 6. Plot of dQ/dt *vs* ΔP for evasion of CO_2 from sea water. Location: 89°42'W, 22°22'N; depth: 25 fathoms; time 0010 local; weather: clear, wind speed 3–5 knots, wind direction SE; sea surface: calm; sea surface temperature: 23°C; chlorinity: 20.2⁰/₀₀.

by Bohr and in this study; and the rapid rate in a system under vigorous agitation, as determined by Guyer and Tobler and in this study. The field values obtained lie in a region between those derived from mild agitation and those obtained by vigorous mixing.

In this study, the air phase in each case was maintained at a homogeneous level, and the exchange rates were determined under various degrees of turbulence of the water. It is apparent that the rate of replacement of the surface water film, as controlled by the water phase, is the dominant factor in determining the rate of transfer of CO_2 through the water interface. Vigorous agitation of the air phase, simulating wind conditions in a storm, would doubtless increase the rate of transfer of CO_2, but whether this would be due to the concurrent increased turbulence of the water and/or increased contact surface with the air phase would be difficult to evaluate. Calculations based on Craig's

TABLE II. LABORATORY STUDIES OF THE RATE CONSTANTS FOR TRANSFER OF CO_2 THROUGH SEA WATER.

	α (mg/cm^{-2}/atm^{-1}/min^{-1})	K min^{-1}	α (cm/min^{-1})
Invasion of CO_2 at Sea (Exp. 1)	1.94	0.062	0.90
Invasion of CO_2 at Sea (Exp. 2)	0.91	0.029	0.45
Evasion of CO_2 at Sea	1.38	0.044	0.64
Bohr	0.26	—	0.121
Becker	0.033	—	0.017
Miyake and Hamada	0.020	—	0.011
Guyer and Tobler	6.6	—	3.6
This Study	0.32	0.007	0.168

(1957) estimate of a seven year residence time for CO_2 in the atmosphere indicate an average transfer rate of 1.77×10^{-4} mg/cm^{2}min for all oceans. Large variations in exchange rate doubtless occur both geographically and spacially. The invasion rate constant, or the rate at which CO_2 transfers from the atmosphere to the sea water, has been found by laboratory experiments to range from 0.033 mg/cm^2, atmosphere/min for a static water system (Becker, 1924) to 6.6 for a vigorously agitated solution (Guyer and Tobler, 1934). For the most part the actual conditions encountered at sea would be intermediate between these values and would vary considerably at one location over a short period of time; the rate at a given location at a given time would depend upon turbulent or advective diffusion processes at the sea-air interface. The values reported here, while valid for only conditions encountered in the experimental method, appear to represent minimal invasion rates for CO_2 under the sea conditions existing at the time.

It is interesting to note that, by using the transfer rate values for the invasion coefficient (Table II) with the average rate constants established by Craig, we obtained a value for partial pressure of CO_2 in the atmosphere necessary to maintain this average transfer rate. This calculation gives partial pressures (in atmospheres) that range from $8,850 \times 10^{-6}$ to 550×10^{-6} for laboratory data, and from 100×10^{-6} to 130×10^{-6} for field data. If these experimental values are near the average for the ocean as a whole, then the data indicate more rapid invasion of CO_2 than is indicated by the C^{14} method. Since little is known about the dynamics of carbon dioxide transfer or of the carbon dioxide system affecting this transfer, it is not surprising to find discrepancies between the completely independent methods. Further work in this area to determine the factors that affect the rate of CO_2 transfer through the sea-air interface both in the laboratory and in the field is certainly warranted. A further step would be to measure the exchange rates for many ocean areas of the world; from such observations a basis would be provided for the calculation of residence time of CO_2 in the atmosphere by a method independent of C^{14} measurements.

Summary and Conclusions. The radioactive tracer techniques have been found useful in the laboratory to measure effectively the exchange rates of CO_2 between the air and sea water. The use of tracers in very high specific activity permits measurements without grossly upsetting the equilibrium, retaining a driving force of the same order of magnitude as that encountered in nature.

The value for α, determined at sea with normal carbon dioxide and continuous nondestructive infrared analysis, has few nonmeasureable and uncontrollable parameters. Therefore, the measured values should be reliable. By using a small closed atmosphere, the direct effect of wind stress and the turbulence in the air phase are reduced significantly; however, the turbulence in the water, except for small surface effects, should be similar to that in an unconfined area.

The experimental design in the laboratory and the empirical nature of the calculations allow room for criticisms as to the meaning of the results when applied to the open ocean. However, the laboratory and field methods may be combined to produce a consistent system that provides data useful in gaining some insight into the actual invasion-rate constant for carbon dioxide over the oceans.

The data presented indicate that the invasion coefficient for CO_2 in the ocean will be affected by turbulence of the air-water interface. The value of α will reflect the turbulent diffusivity of the water phase, and perhaps in some cases, that of the gas phase. From the results obtained in these experiments, the transfer rate is controlled by a first order reaction, probably due to the turbulence of the water film. Further studies are needed, however, to ascertain the importance of air versus water turbulence in the transfer process.

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