

A NEW EXPERIMENTAL TECHNIQUE FOR VALIDATING EXCHANGE MODELS OF CARBON DIOXIDE BETWEEN THE ATMOSPHERE AND SEA-WATER

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Summary—The mechanism of CO₂-exchange between the atmosphere and sea-water was re-examined by simultaneously measuring pH and pO₂ in artificial sea-water exposed to CO₂ and air atmospheres. The data were fitted to an exchange model by using both the differential and integral forms of the diffusion equation. It was found that the pH and pO₂ data support the assumption that the exchange for these gases is driven by the gradient of the partial pressure of the gas across the imaginary solution-gas boundary layer (the *z* layer) and is not affected by chemical reaction or hydration rate under the experimental conditions used, *viz.* 1–100 meq/l., alkalinity, pH 4.5–8.3 and *z*-layer thickness 2–500 μm. It is concluded that the rate of hydration of CO₂ plays an insignificant role in the exchange mechanisms between the atmosphere and the oceans.

Exchange of CO₂ between the gas and liquid phases is a fundamental process in many scientific and technological disciplines. The process is crucial in regulating CO₂ concentration in the oceans and atmosphere, a topic which has recently been of much concern in connection with the very high production of CO₂ due to the utilization of fossil fuel by modern technology.^{1,2} The fact that dissolved CO₂ undergoes hydration to produce carbonic acid and that the acid further dissociates into bicarbonate and carbonate ions, raises the question of possible effects of these reactions on the exchange process. The simplified model generally used to describe gas exchange between the gas and liquid phases is the film model.³ It consists of an imaginary stagnant solution layer (the *z* layer) separating the gas phase from the bulk of solution, both of which are assumed to be well mixed. The exchange process between the two phases is thus assumed to be controlled by molecular diffusion of the dissolved gas through the *z* layer. In the case of CO₂, this simple model is complicated by the fact that CO₂ reacts with the water and the transport process might therefore be dependent on the hydration kinetics as well as the migration rates of a number of species, such as HCO₃⁻ and CO₃²⁻. A number of investigators have studied this question analytically and experimentally. The proposed methods differ with regard to the assumptions made concerning the carbonate chemistry within the layer. Bolin,⁴ and Hoover and Berkshire⁵ assumed the pH to be constant within the layer, Quinn and Otto⁶ assumed electroneutrality, whereas Emerson's approach^{7,8} permitted alkalinity and ionic gradients within the *z* layer. The different models predict similar behaviour: a transport rate which is dependent on pH and the thickness of the boundary layer. Attempts to verify

the proposed models experimentally were made by Hoover and Berkshire⁵ and Liss.⁹ In both cases exchange of CO₂ was monitored by tagging the dissolved CO₂ with ¹⁴C and monitoring the residual radioactivity in solution after loss of CO₂ to the atmosphere. The experiments were done with solutions buffered at low and high pH (~5 and ~8 respectively).

It is questionable whether the experimental procedures used in previous studies are capable of simulating natural processes, for at least two reasons. First, it is unknown whether a tracer diffusion (¹⁴CO₂) is indeed quantitatively equal to bulk diffusion of CO₂.¹⁰ Secondly, application of a buffer to control the pH introduces an artificial restriction not found in natural environments such as oceans and lakes, in which the pH is mainly controlled by the carbonate system.¹⁰ A constant pH implies a constant H₂CO₃/HCO₃⁻ ratio independent of total CO₂ in sea-water, which is contrary to the behaviour of the oceans. Consequently, the results of these experiments may not reflect the actual behaviour of a solution such as sea-water in which the carbonate system is the main buffer. The purpose of the present study was to examine the process of CO₂ exchange between the atmosphere and sea-water over a large pH range under solution-chemistry conditions which simulate those of the oceans. This was accomplished by measuring simultaneously the partial pressures of CO₂ and O₂ in sea-water solutions which were exposed to overlying atmospheres of air and CO₂. The purpose of simultaneously monitoring pO₂ and pCO₂ was to permit the comparison of an inert gas (O₂ under these exchange conditions) and a chemically reactive gas (CO₂).

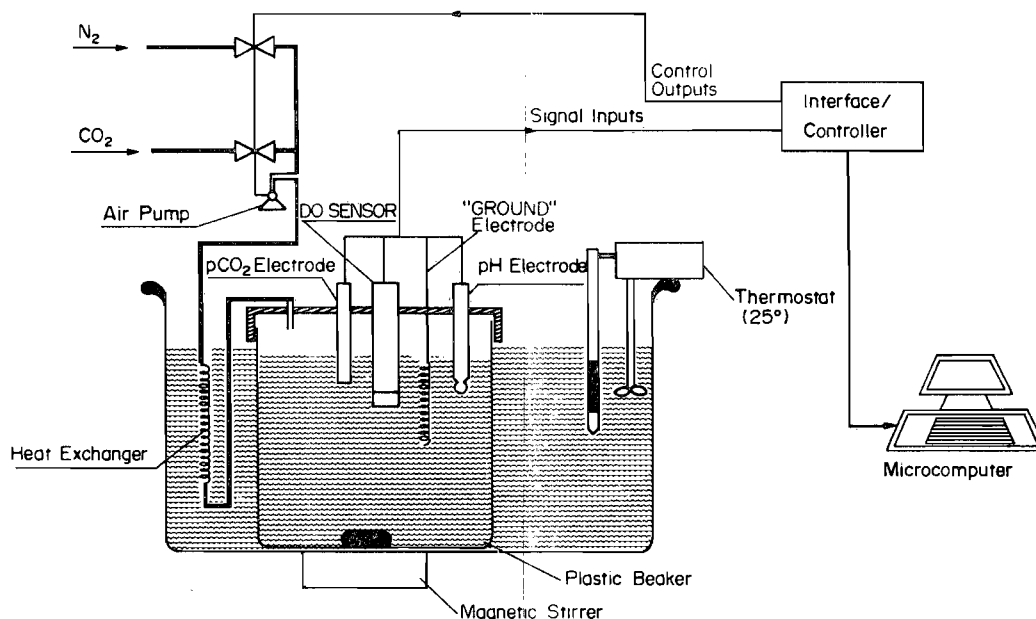


Fig. 1. Experimental assembly (DO SENSOR = dissolved oxygen sensor).

EXPERIMENTAL

The apparatus (Fig. 1) consisted of a covered beaker kept at constant temperature, pH and dissolved-oxygen electrodes, and a computerized data-acquisition system.¹¹ The experiments were done at 25° on 2-litre samples of artificial Mediterranean sea-water¹² with alkalinity in the range 1–100 meq/l. The solutions, stirred by a magnetic stirrer, were exposed to a CO₂ and air atmosphere at atmospheric pressure (ca. 980 mbar) and the resulting changes in pH and dissolved O₂ were monitored, with reading every 0.5–2 min. In some experiments, the exchange between the gas and liquid phases was accelerated by bubbling the gas through the solution. The pH change during the experimental runs was from pH 4.5 to pH 8.3. The dissolved-oxygen electrode was similar in design to the one described earlier.^{13,14} The membrane was a 2.4×10^{-3} cm (1 mil) thick Teflon film.

In some experiments pCO₂ was also measured directly with a membrane electrode (ORION, type 9502), but the results were not used in the regression analysis.

RESULTS AND DISCUSSION

The partial pressure of CO₂ (pCO₂) and concentration of total CO₂ (TCO₂) solution, during the experimental runs, were calculated from the carbonate alkalinity and pH by using the apparent constants of the carbonate system at the given salinity:¹⁰

$$pCO_2 = \frac{CA \times a_H^2}{K_1 \alpha_s [a_H + 2K_2]} \quad (1)$$

and

$$TCO_2 = CA \left[\frac{a_H K_1 + K_1 K_2 + a_H^2}{a_H K_1 + 2K_1 K_2} \right] \quad (2)$$

where CA = carbonate alkalinity; K_1 = first apparent dissociation constant of carbonic acid, K_2 = second apparent dissociation constant of carbonic acid, α_s = solubility of CO₂, a_H = hydrogen-ion activity.

The CO₂ and O₂ data for the transition from low to high pH (Fig. 2), were fitted to the simple gas-exchange model:³

$$\frac{dC}{dt} = -\frac{D_c}{z} (pc_b - pc_s) \alpha_c A / V \quad (3)$$

where C = concentration of the gas (mole/ml), D_c = diffusion coefficient of the gas c (cm²/sec), z = thickness of stagnant diffusion layer (cm), α_c = solubility of the gas c (mole·cm⁻³·atm⁻¹), pc = partial pressure of gas c (atm), A = area of the solution (cm²) in direct contact with the atmosphere, V = volume of solution (cm³) and the subscripts b and s denote the bulk solution and boundary layer respectively.

The model assumes that the driving force of the exchange process is dependent on the partial-pressure gradient of the pertinent gas across the z layer (or the

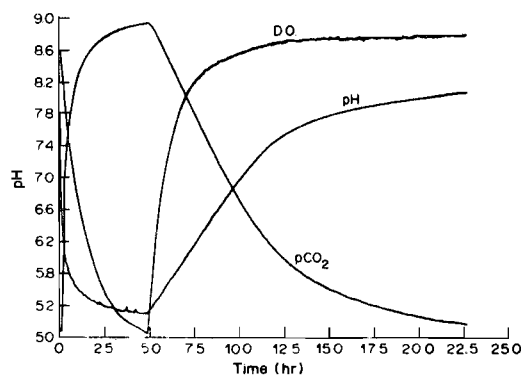


Fig. 2. Typical response of pH, pO₂ and pCO₂ of solutions to a change in the overlying atmosphere, in the sequence air-CO₂-air.

concentration gradient of $H_2CO_3^* = [CO_2(aq) + H_2CO_3]$ and neglects kinetic effects, and migration of ionized species such as HCO_3^- . It is also assumed that pCO_{2b} at any instant can be calculated from the pH and carbonate alkalinity. That means that hydration and ionization-rate effects are assumed to be insignificant in comparison with the overall time constant of the exchange process, *i.e.*, the carbonate system in the bulk solution can be considered to be in equilibrium at any instant.

The explicit equations for O_2 and CO_2 exchange are:

$$\frac{dO_2}{dt} = -\frac{D_{O_2}\alpha_{O_2}}{zh} pO_{2b} + \frac{D_{O_2}\alpha_{O_2}}{zh} pO_{2s} \quad (4)$$

$$\frac{dTCO_2}{dt} = -\frac{D_{CO_2}\alpha_{CO_2}}{zh} pCO_{2b} + \frac{D_{CO_2}\alpha_{CO_2}}{zh} pCO_{2s} \quad (5)$$

where

$$O_2 = pO_{2b}\alpha_{O_2} \quad (6)$$

and h = height of solution in beaker (Fig. 1).

The parameters D/z and pc_s were estimated for each experimental run by fitting the data to the linear equation:

$$y = ax + b \quad (7)$$

where $y = dTCO_2/dt$, $x = pc_b$, $a = -D_c\alpha_c/zh$, $b = D_c\alpha_c pc_s/zh$, from which we obtain

$$\frac{D_c}{z} = \frac{ah}{\alpha_c}$$

and

$$pc_s = b/a$$

where c denotes O_2 or TCO_2 .

The derivatives for each point were obtained by using a modified numerical differentiation method with an inherent smoothing effect,^{15,16} to reduce differentiation noise. The equation for the i th value for a backward numerical differentiation was established as

$$\frac{dC}{dt}(i) = \frac{1}{10t_s} [-2C(i-2) - C(i-1) + C(i+1) + 2C(2+i)] \quad (8)$$

where t_s is the sampling time.

A second approach to reduce the fitting scatter further was also used. It was based on the integral form of equations (4) and (5), which can be represented by:

$$TC = -\frac{D\alpha_c}{zh} \int pc_b dt + \frac{D\alpha_c}{zh} pc_s \int dt \quad (9)$$

or, in its numerical form:

$$TC_i = -\frac{D\alpha_c}{zh} \sum_0^i pc_{b,i} + \frac{D\alpha_c}{zh} pc_s \sum_0^i i \quad (10)$$

In this case, the data were fitted to a two-variable

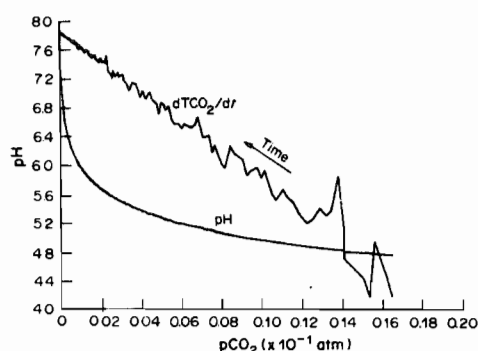


Fig. 3. Typical regression of $dTCO_2/dt = f(pCO_{2b})$ in the derivative form.

equation of the form:

$$y = ax_1 + bx_2 \quad (11)$$

with

$$y_i = TC_i,$$

$$x_{1i} = \sum_0^i pc_{b,i},$$

$$x_{2i} = \sum_0^i i,$$

$$a = D\alpha_c/zh,$$

$$b = D\alpha_c pc_s/zh.$$

Typical fitting curves for the differential and integral forms are depicted in Figs. 3 and 4.

The data from all the experiments were found to fit the simple model of equation (1) for both O_2 and CO_2 , which assumes that the flux is controlled solely by the partial-pressure gradient between the solution and gas phases (Tables 1 and 2). The excellent fit of the data to the model suggests that kinetic effects associated with the hydration rate of CO_2 are negligible over the range of conditions used in the experiments. It was found that by using this model along with the derived numerical values of D_{CO_2}/z for a given experiment, the change in TCO_2 during the experimental cycle can be accurately simulated (Fig.

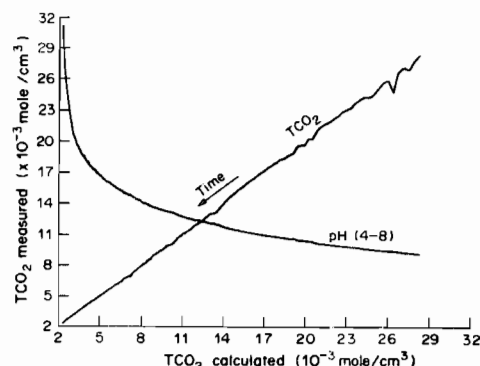


Fig. 4. Measured TCO_2 vs. predicted (TCO_2 calculated) during a typical experimental run.

Table 1. Summary of experimental results for O₂ exchange

Experiment	Gas		Alkalinity meq/l.	pH range	D_{O_2}/z^* , $10^{-3}cm/sec$	Correlation coefficient, R^2	Confidence limits†, %	$z\ddagger$, μm
	Atmosphere	Flow						
1	Air	Surface	10	5.4-7.0	2.88 ± 0.04	0.9918	> 99	73.6
1	CO ₂	Surface	10	5.6-7.8	2.62 ± 0.22	0.9920	> 20	80.9
2	Air	Surface	1	4.7-6.4	2.80 ± 0.07	0.9731	> 95	75.7
2	CO ₂	Surface	1	4.8-4.9	3.13 ± 0.37	0.9395	> 80	67.7
3	Air	Bubbles	1	4.4-5.7	38.7 ± 1.0	0.9930	> 90	5.56
3	CO ₂	Bubbles	1	4.4-7.4	45.6 ± 0.8	0.9976	> 80	4.64
4	Air	Bubbles	10	5.4-7.1	70.3 ± 4.6	0.9795	> 50	3.01
4	CO ₂	Bubbles	10	5.4-6.5	104.4 ± 2.9	0.9924	> 99	2.03
5	Air	Surface	100	6.6-7.8	3.95 ± 0.06	0.9940	> 98	53.7
5	CO ₂	Surface	100	6.6-7.1	7.53 ± 0.13	0.9968	> 80	28.2

* Limits are $\pm 2\sigma$.† Based on χ^2 test.‡ Assuming $D_{O_2} = 2.12 \times 10^{-5} cm^2/sec$.

4). We conclude therefore that this model represents to a high degree of accuracy the process of gas exchange for both CO₂ and O₂. It is also found that the diffusion coefficients of the two gases (when expressed as a function of partial pressures) is numerically identical, within 3% (Table 3).

Rigorous statistical analysis of typical experimental runs did not reveal any significant difference between the data points at low pH and those at high

pH (Table 4). Such a difference should have been observed if previously suggested models were accepted.^{4,5}

The results of the present study seem to conflict with the conclusions of previous investigations although a direct comparison between our data and previous results is impossible owing to the difference in the experimental techniques used. Previous studies seem to suggest that a kinetic enhancement should be

Table 2. Summary of experimental results for CO₂ exchange

Experiment	Gas		Alkalinity meq/l.	pH range	D_{CO_2}/z^* , $10^{-3}cm/sec$	Correlation coefficient, R^2	Confidence limits†, %	$z\ddagger$, μm
	Atmosphere	Flow						
1	Air	Surface	10	5.4-8.0	2.63 ± 0.02	0.9926	> 90	73.6
1	CO ₂	Surface	10	5.6-7.8	3.16 ± 0.47	0.8224	> 0.1	80.9
2	Air	Surface	1	4.7-7.8	2.64 ± 0.02	0.9890	> 99	75.7
2	CO ₂	Surface	1	4.8-4.9	5.24 ± 1.60	0.6930	> 80	67.7
3	Air	Bubbles	1	4.3-7.6	35.2 ± 0.11	0.9990	> 98	5.56
3	CO ₂	Bubbles	1	4.4-7.4	48.6 ± 2.2	0.9984	> 95	4.64
4	Air	Bubbles	10	5.4-8.3	69.7 ± 0.25	0.9990	> 99	3.01
4	CO ₂	Bubbles	10	5.4-6.5	113.9 ± 3.1	0.9926	> 50	2.03
5	Air	Surface	100	6.6-8.3	3.71 ± 0.03	0.9906	> 95	53.6
5	CO ₂	Surface	100	6.6-7.1	5.38 ± 0.63	0.8809	> 5	28.1
6	Air	Surface	2.4	4.9-7.9	0.41 ± 0.001	0.9999	> 99	485‡

* Limits are $\pm 2\sigma$.† Based on χ^2 test.‡ Calculated from O₂ data assuming $D_{O_2} = 2.12 \times 10^{-5} cm^2/sec$.‡ Assuming $D_{CO_2} = 1.97 \times 10^{-5} cm^2/sec$.Table 3. Calculated ratio of O₂ and CO₂ diffusion coefficients

Experiment	Gas		Alkalinity meq/l.	$D_{O_2}/D_{CO_2}^*$	$z\ddagger$, μm
	Atmosphere	Flow			
1	Air	Surface	10	1.09 ± 0.02	73.6
1	CO ₂	Surface	10	0.82 ± 0.14	80.9
2	Air	Surface	1	1.06 ± 0.02	75.7
2	CO ₂	Surface	1	0.59 ± 0.20	67.7
3	Air	Bubbles	1	1.08 ± 0.03	5.56
3	CO ₂	Bubbles	1	0.93 ± 0.05	4.64
4	Air	Bubbles	10	1.00 ± 0.07	3.01
4	CO ₂	Bubbles	10	0.91 ± 0.04	2.03
5	Air	Surface	100	1.06 ± 0.02	53.7
5	CO ₂	Surface	100	1.39 ± 0.17	28.2

* Limits are $\pm 2\sigma$.† Assuming $D_{O_2} = 2.12 \times 10^{-5} cm^2/sec$.

Table 4. Statistical analysis of data sections of experiments 1 and 2, for surface flow of air, to examine possible variation of D as a function of pH.

Experiment	Alkalinity, meq/l.	No. of points	pH range	$D_{\text{CO}_2/z}$, $10^{-3} \text{ cm}^2/\text{sec}$	Correlation coefficient, R^2	Confidence limits, † %	F-test, %	z §, μm
1	10	150	5.4–6.9	2.62 ± 0.05	0.9880			73.6
1	10	150	6.9–7.8	2.70 ± 0.05	0.9862			73.6
1	10	150	7.8–8	2.34 ± 0.60	0.2883			73.6
1	10	450	5.4–8	2.62 ± 0.03	0.9880	> 90	< 10	73.6
2	1	160	4.7–6.4	2.64 ± 0.06	0.9828			75.7
2	1	160	6.4–7.3	2.61 ± 0.06	0.9809			75.7
2	1	160	7.3–7.8	3.64 ± 1.37	0.1524			75.7
2	1	480	4.7–7.8	2.64 ± 0.03	0.9828	> 95	< 10	75.7

* Limits are $\pm \sigma$,† Based on χ^2 test,§ Assuming $D_{\text{O}_2} = 2.12 \times 10^{-5} \text{ cm}^2/\text{sec}$.

observed at high pH for experiments with a z layer about $300 \mu\text{m}$ thick. Our results do not support such a conjecture, as we did not observe any difference between the results for high and low pH even for a z layer about $500 \mu\text{m}$ thick. Therefore, the question of kinetic enhancement can be excluded in discussion of CO_2 exchange between the atmosphere and the oceans, for which the z layer has been estimated to be in the range $30\text{--}70 \mu\text{m}$ thick.^{17,18} Hence the only CO_2 flux that should be considered in this case is the one directly associated with, and linearly proportional to, the pCO_2 gradient across the z layer. However, the time constant of the response of the oceans to change in atmospheric pCO_2 will none the less be dependent on the chemical reactivity of CO_2 in sea-water.¹⁹ As a result of hydration of CO_2 and subsequent ionization, the increase in pCO_2 due to CO_2 invasion is much smaller for the pH range of normal sea-water than the increase at low pH. It can be calculated, for example, that at pH 8.2 an increase of $1 \mu\text{mole/l}$. in the TCO_2 concentration in sea-water will result in an increase of 2.2 ppm in pCO_2 , whereas the same increase in TCO_2 will cause a change of 36 ppm in pCO_2 at pH 5. Consequently, the decrease in CO_2 flux due to increase in TCO_2 in the ocean will be slower, reducing the time required for reaching equilibrium.

Although the experimental results of the present study disagree with the results of previous investigations, the general conclusion concerning the minor effect of hydration rate on exchange of CO_2 between the atmosphere and the oceans, has already been stated by a number of investigators. The estimated thickness of the z layer in the oceans is about $70 \mu\text{m}$, for which previous models also suggest a negligible kinetic enhancement. However, augmentation of the hydration rate could be important in other areas. It has been suggested, for example, that reflux of CO_2 from the urinary tract to the blood could be highly dependent on the kinetics of hydration of CO_2 .²⁰ In this case, the thickness of the

membranes through which the CO_2 diffuses is considerably larger than that of the z layer in the oceans, and the effect of rate of hydration could be important. A better assessment of the exchange mechanism may be obtainable when more experimental data for thick diffusion layers are available.

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