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Carbon Dioxide–Oxygen Separation: Facilitated Transport of Carbon Dioxide across a Liquid Film

Abstract. *An immobilized film of an aqueous bicarbonate-carbonate solution was developed which was 4100 times more permeable to carbon dioxide than to oxygen. The carbon dioxide transport was reaction-rate limited, and thus it could be increased by addition to the film of catalysts for the hydrolysis of carbon dioxide.*

The steady-state transport of carbon dioxide across an aqueous film is increased if there is a concentration difference in bicarbonate cross the film (*1*). Presumably a carrier transport mechanism is operative in this process as it is in the transport of oxygen in aqueous hemoglobin solutions (*2*). The mechanism of facilitated carbon dioxide transport in bicarbonate solutions has not been elucidated in detail. We studied the transport of carbon dioxide across thin films of concentrated aqueous carbonate-bicarbonate solutions. The work led to a better understanding of carbon dioxide transport in this system, and to the development of an "immobilized" liquid membrane which is highly selective for carbon dioxide and is suitable for removal of carbon dioxide in a closed life-supporting environment.

Because of its high carbon dioxide solubility water is an obvious choice as a membrane for separation of carbon dioxide and oxygen, and it has better permeation characteristics for this application than any polymeric material. The carbon dioxide permeability of pure water is 210×10^{-9} cm^3(STP)·cm/sec cm^2 cm-Hg (*3*), and the carbon dioxide–oxygen separation factor (ratio of carbon dioxide permeability to oxygen permeability) is 22. For an immobilized film of water we selected a porous cellulose acetate film similar to that made for a reverse osmosis process for desalination (*4*). The membrane contained 60 percent water; it was 0.007 cm thick, and it had carbon dioxide and oxygen permeabilities of 40×10^{-9} and 2×10^{-9}, respectively. Compared with a film of pure water, the effective area for permeation in the cellulose acetate film was decreased very roughly by a factor of 1.7; thus the diffusion coefficients were lowered approximately by a factor of 3.

To increase the carbon dioxide permeability of the immobilized liquid film we considered methods of establishing a difference in concentration in bicarbonate across the film. The relation at equilibrium among carbon dioxide, bicarbonate, and carbonate is

$$C_2 = K(C_1)^2/C_3 \tag{1}$$

where C is concentration (mole/cm^3) and subscripts 1, 2, and 3 refer here and in subsequent equations to bicarbonate, carbonate, and carbon dioxide, respectively. At 25°C the value of K is approximately 1.3×10^{-4} (*5*). In the proper range of carbon dioxide concentrations and for bicarbonate and carbonate concentrations of the order of moles per liter, a bicarbonate-carbonate film across which there is partial pressure difference in carbon dioxide may have large and opposing concentration differences in bicarbonate and carbonate. The total flux of carbon dioxide across such a film, which is equal to the total flux of carbon at any point in the film, is

$$N_3{}^T = N_1 + N_2 + N_3 \tag{2}$$

where N is mass flux (mole/sec cm^2). Expressions for the flux of the species present in the film are (*6*)

$$\begin{aligned} N_3 &= -D_3\left(\frac{\partial C_3}{\partial x}\right) \\ N_1 &= -D_1\left(\frac{\partial C_1}{\partial x} - \frac{C_1F}{RT}\cdot\frac{\partial\varphi}{\partial x}\right) \\ N_2 &= -D_2\left(\frac{\partial C_2}{\partial x} - \frac{2C_2F}{RT}\cdot\frac{\partial\varphi}{\partial x}\right) \\ N_4 &= -D_4\left(\frac{\partial C_4}{\partial x} + \frac{C_4F}{RT}\cdot\frac{\partial\varphi}{\partial x}\right) \end{aligned} \tag{3}$$

where subscript 4 refers to the cations, D is diffusivity (cm^2/sec), F is Faraday's constant in cal/volt equivalents, R is the gas constant in cal/deg mole, φ is electrical potential in volts, and x is distance into the film in centimeters. If the effect of small concentrations of hydrogen and hydroxide ions is neglected, at steady state the following relations obtain

$$N_1 + 2\,N_2 = 0 \tag{4}$$

$$N_4 = 0 \tag{5}$$

and at all points in the film

$$C_4 = C_1 + 2\,C_2 \tag{6}$$

If the diffusivities of bicarbonate and carbonate are equal, which is a good approximation, then by differentiating Eq. 6 with respect to x and combining it with Eqs. 3 to 5, it can be shown that the potential gradient

$$\frac{\partial\varphi}{\partial x} = 0 \tag{7}$$

Thus there is no potential difference across the film if the diffusivities of bicarbonate and carbonate are equal. Assuming that $\partial\varphi/\partial x$ is zero and substituting Eq. 3 into Eq. 2, the expression for the total flux of carbon dioxide $N_3{}^T$ is

$$N_3{}^T = \frac{D_3(C_3{}^0 - C_3{}^L)}{L} + \frac{D_1}{2}\cdot\frac{(C_1{}^0 - C_1{}^L)}{L} \tag{8}$$

where superscripts 0 and L refer to the high-pressure and low-pressure sides of the film, respectively. In the following discussion we assume that the diffusivities of carbonate and bicarbonate are equal. If, in fact, they differed by as much as 20 percent, the effect on the total flux of CO$_2$ would be negligible, and the conclusions which are stated below would be unaltered.

Equation 8 is useful if one knows C_1^0 and C_1^L in terms of C_3^0 and C_3^L (the latter terms are assumed to be known). If we assume that all reacting species are present in equilibrium concentrations, then the surface concentration of bicarbonate can be calculated from Eq. 1. If this assumption is correct, then the second term on the right-hand side of Eq. 8 may be orders of magnitude larger than the first.

We measured the permeabilities of carbon dioxide and oxygen in porous cellulose acetate films impregnated with saturated (6.4*N*) cesium bicarbonate solutions (cesium bicarbonate being the most soluble alkali bicarbonate). The films were prepared by soaking porous cellulose acetate membranes in bicarbonate solutions for at least 1 day. For measuring permeabilities of the films, they were backed by a 0.5-mil silicone rubber membrane to avoid forcing the solution out of the cellulose acetate matrix when a pressure difference was applied. The resistance of the silicone rubber membrane to oxygen and carbon dioxide permeation was known, and it was small compared to the porous cellulose acetate resistance. The composite film was supported on a porous stainless steel disk so that any desired pressure difference could be maintained across the film. Over the high-pressure side of the film a moist gas mixture of 5 percent carbon dioxide and 95 percent oxygen was circulated. The low-pressure side of the film was maintained at a constant pressure in the range of 2.5 to 4 cm total pressure. The gas on the low-pressure side of the film passed through a controlled leak valve and then into a vacuum system. The rate at which gas passed through the leak valve was determined by allowing the gas passing through the leak valve to build up a pressure in the vacuum system of approximately 200 μ-Hg over a measured interval. This small change in pressure did not alter the pressure on the low-pressure side of the film, and thus, steady-state operation was sustained while the rate was being determined. The composition of the permeating gas was determined by sampling the gas from the vacuum system and analyzing on a mass spectrometer. The system required approximately 1 hour to reach steady state. Permeation measurements on a given film were made over a period of up to 5 days. The partial pressure of carbon doxide on the low-pressure side of the film was varied from 0.4 to 2.0 cm-Hg. Within this range there was no appreciable variation in the carbon dioxide permeability and carbon dioxide–oxygen separation factor, and the average of all of the results obtained was that the permeability of carbon dioxide was 75×10^{-9}; that of oxygen was 0.05×10^{-9}, and the carbon dioxide–oxygen separation factor α was 1500. This separation factor was hundreds of times higher than any achieved previously.

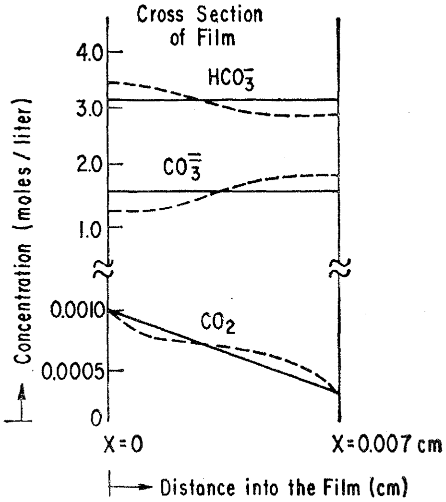

Fig. 1. Concentration profiles in a bicarbonate-carbonate film, across which a carbon dioxide concentration difference is maintained. The solid lines are for reactions shown by Eqs. 9 and 10 being very slow compared with the rate of diffusion of carbon dioxide across the film. The effect of increasing the rate of either of these reactions is illustrated by the dotted lines.

The effect of the cesium bicarbonate–carbonate mixture in the film was to lower the oxygen permeability by a factor of 40 and to raise the carbon dioxide permeability by a factor of 2. Let us consider first the oxygen results. The viscosity of a saturated cesium bicarbonate solution is twice that of pure water. Thus the diffusivity of a solute in the cesium bicarbonate solution is approximately one-half the diffusivity in pure water. This would mean that the solubility of oxygen in the cesium bicarbonate–carbonate film must be twenty times less than the solubility of oxygen in water. The ionic strength of the solution in the film was approximately 8, and in such a solution this large salting out effect is not unreasonable (*7*).

In order to compare the carbon dioxide permeability with Eq. 8 it will be assumed that all species are present in equilibrium concentrations. Diffusion coefficients in the porous cellulose acetate film impregnated with water were three times lower than diffusion coefficients in pure water. The salt in the film further lowered the diffusion coefficients approximately by a factor of 2. Thus the diffusion coefficient of carbon dioxide, which, in pure water is 2×10^{-5} cm²/sec, was approximately 3×10^{-6} in the porous cellulose acetate film impregnated with saturated cesium bicarbonate. It is assumed that the diffusion coefficients of bicarbonate and carbonate are also 3×10^{-6} cm²/sec. A reasonable estimate of the carbon dioxide solubility in the film is 0.02 mole/liter at 1 atmosphere of carbon dioxide over the solution (*8*). The K of Eq. 1 is 1.3×10^{-4} (*5*). Permeabilities were lowered by a factor of 1.7 because of the blocking of the effective area for permeation by the polymer. From the above constants and a partial pressure of carbon dioxide on the high-pressure and low-pressure sides of the film of 3.4 and 0.4 cm-Hg, respectively, the carbon dioxide flux from Eq. 8, divided by 1.7, is 3.82×10^{-7} mole/sec cm², which corresponds to a carbon dioxide permeability of $22{,}900 \times 10^{-9}$. For a partial pressure of carbon dioxide on the low-pressure side of 2.1 cm-Hg, Eq. 8 leads to a permeability of $15{,}100 \times 10^{-9}$.

Equation 8 is a simplified picture of the transport processes in the film, and, in addition, the values of the constants used to predict the carbon dioxide permeability are not accurately known. However, one would not expect the predicted carbon dioxide permeability to be hundreds of times higher than the experimental value. Thus the assumption made in applying Eq. 8, that of chemical equilibrium among all reacting species, was incorrect. One or more of the reactions occurring in the film must have been slow compared with the rate of diffusion. The three principal reactions occurring in the film are (*9*)

$$CO_2 + H_2O \underset{k''_1}{\overset{k'_1}{\rightleftarrows}} H^+ + HCO_3^- \qquad (9)$$

$$CO_2 + OH^- \underset{k''_2}{\overset{k'_2}{\rightleftarrows}} HCO_3^- \qquad (10)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--} \qquad (11)$$

where the k's are reaction rate constants. The reactions shown by Eqs. 9 and 10 are measurably slow, and their rates, mechanisms, and catalysis have been studied many times (*9*). The reaction shown by Eq. 11 is essentially instantaneous.

On the side of the film exposed to a high partial pressure of carbon dioxide (side 1) reactions shown by Eqs. 9 and 10 tend to go to the right, and that of Eq. 11 tends to go to the left. Thus, carbon dioxide is consumed near this surface of the film, and the flux of carbon dioxide into the film is more rapid than it would be in the absence of any reaction. These reactions tend to occur in the reverse direction at the side of the film exposed to a low partial pressure of carbon dioxide (side 2). Near side 1 bicarbonate is produced; it diffuses across the film, and near side 2 it decomposes to produce carbon dioxide. Near side 2 carbonate is produced, it diffuses across the film, and near side 1 it is consumed. To maintain zero current flow, the flux of bicarbonate must be twice the absolute value of the flux of carbonate. Thus carbon dioxide transport across the film is augmented or facilitated by the diffusion of bicarbonate.

Qualitatively, the effect of the rates of reactions shown by Eqs. 9 and 10 on the concentration profiles within a concentrated bicarbonate–carbonate film, across which there is a carbon dioxide concentration gradient is shown in Fig. 1. When all reacting species are present in equilibrium concentrations (very fast reactions) then there are concentration differences in bicarbonate and carbonate across the film of the order of moles per liter. The other extreme of very slow reactions is shown in the solid lines of Fig. 1. Here, there is essentially no concentration difference in bicarbonate or carbonate, and the carbon dioxide profile is linear. The dotted lines of Fig. 1 are for the case where the rate of reaction shown by Eqs. 9 or 10 is sufficiently large that the carbon dioxide concentration profile is nonlinear, and there is a discernible concentration difference in bicarbonate and carbonate across the film.

To predict the total carbon dioxide flux across the film a differential mass balance on carbon dioxide at any point in the film is written

$$D_3 \frac{\partial^2 C_3}{\partial x^2} = k'_1 C_3 - k''_1 C_5 C_1 + k'_2 C_3 C_6 - k''_2 C_1 \qquad (12)$$

where subscripts 5 and 6 refer to hydrogen and hydroxide ion, respectively. Equation 12 can be considerably simplified by considering the order of magnitude of the concentration difference in bicarbonate across the film in the present experiment. If all of the carbon dioxide transport is in the form of bicarbonate, and the diffusion coefficient of bicarbonate is of the order of 10^{-6} cm²/sec, then the concentration difference of bicarbonate must be of the order of 10^{-2} mole/liter, a small value compared with the absolute value of the average bicarbonate concentration. In solving Eq. 12 the concentration of bicarbonate can be considered a constant. Thus the concentrations of H^+ and OH^- are also constant, and the only dependent variable in Eq. 12 is the concentration of carbon dioxide. The appropriate boundary conditions are the concentration of carbon dioxide at the two sides of the film, and the solution of Eq. 12 is

$$C_3 = K_1 \sinh (Kx) + K_2 \cosh (Kx) + K_3 \qquad (13)$$

where the K's are constants involving the system parameters.

The flux of dissolved carbon dioxide (not the total flux of carbon dioxide) at any point in the film is

$$N_3 = - D_3 \frac{\partial C_3}{\partial x} = - D_3(K_4 \cosh Kx + K_5 \sinh Kx) \qquad (14)$$

where the K's are constants involving the system parameters. The total flux of carbon dioxide ($N_3{}^T$) is the sum of the fluxes of dissolved carbon dioxide, bicarbonate, and carbonate. Since the latter two are zero at the boundaries, the equation for the total flux of carbon dioxide is given by Eq. 14 evaluated at $x = 0$ or $x = L$. That is,

$$N_3{}^T = N_3 \text{ (evaluated at } x = 0 \text{ or } x = L). \qquad (15)$$

If system parameters which are within reason are selected, Eq. 15 leads to a carbon dioxide permeability equal to the experimental value of 75×10^{-9}. Unfortunately, many of the system parameters are not well known, and the real value of Eq. 15 is in predicting at least semiquantitatively the carbon dioxide permeability as a function of key variables such as reaction rates, carbon dioxide partial pressures, and film thickness.

It is clear from the foregoing that the carbon dioxide permeability and the carbon dioxide–oxygen separation factor would be increased by catalyzing the reactions of Eqs. 9 and 10. It is known that, among many other materials, carbonic anhydrase and sodium arsenite catalyze the reaction shown by Eq. 9 (*9*), and we have tested the effect of both of these materials on the carbon dioxide permeability. Porous cellulose acetate films were impregnated with a 2*N* potassium bicarbonate solution containing 2 g of carbonic anhydrase per liter. Initially, the effect of the carbonic anhydrase was to increase the carbon dioxide permeability by approximately a factor of 6, but over a period of several days the permeability decreased almost to its original value. Porous cellulose acetate films were impregnated with a saturated cesium bicarbonate solution containing 0.5*N* sodium arsenite. The experimental conditions were essentially the same as those for the saturated cesium bicarbonate films and the results were that the permeability for carbon dioxide was 214×10^{-9}, the permeability for oxygen was 0.052×10^{-9}, and the separation factor was 4100.

The effect of the sodium arsenite was to increase the carbon dioxide permeability by a factor of 3, and since sodium arsenite is stable this performance could be maintained indefinitely. The oxygen permeabilities in this and in the previous experiment with no catalyst were the same, indicating that the experiments were performed on equivalent films.

The development of this "immobilized" liquid membrane may offer an attractive alternative to existing methods for removal of carbon dioxide from closed, life-supporting environments. For example, with this membrane it will be possible to build a simple, compact, lightweight membrane device with a low power requirement which will concentrate the carbon dioxide present in the atmosphere of a manned spacecraft at approximately 1 to over 95 percent in one passage through the membrane.

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solubility [(cm^3 of gas (STP)/cm^3, cm-Hg)] of the solute in the solvent. The values of the solubility of carbon dioxide and oxygen in water were taken from the *Handbook of Chemistry and Physics*. The values of the diffusivity of carbon dioxide and oxygen in water were taken from L. E. Scriven and R. L. Pigford, *Amer. Inst. Chem. Eng. J.* **4**, 439 (1958), and J. F. Davidson and E. J. Cullen, *Trans. Inst. Chem. Eng. London* **35**, 51 (1957), respectively.
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Carbon-13–Rich Diagenetic Carbonates in Miocene Formations of California and Oregon

Abstract. *Carbon unusually rich in* C^{13} ($\delta C^{13} = +5.4$ *to* $+19.0$ *per mil relative to the Peedee belemnite carbonate standard of the University of Chicago) is characteristic of certain diagenetic limestones and dolomites in the Miocene Monterey Shale of California and the Nye Mudstone of Oregon. This heavy carbon may have originated through low-temperature equilibration between* CO_3^{--} *and* CO_2 *in migrating carbonated waters or between* CH_4 *and* CO_2 *in natural gas. Light carbon* ($\delta C^{13} = -5.6$ *to* -18.2 *per mil) derived through nonequilibrium oxidation of organic matter also occurs in the carbonate of Monterey Shale in some localities, but at most places it is much less common than heavy carbon.*

Carbon in primary marine limestone varies only slightly in its C^{13}/C^{12} isotopic composition, most of the samples falling within the range of $\delta C^{13} = 0 \pm 4$ per mil relative to the Peedee belemnite carbonate standard of the University of Chicago (PDB) (*1–3*). This relative constancy of composition results from precipitation of marine carbonate in isotopic equilibrium with oceanic bicarbonate that is virtually constant isotopically. A few marine organisms secrete carbonate with δC^{13} as light as -9.3 (*4*) or as heavy as $+5.9$ (*5*), but most, including the quantitatively important pelagic Foraminifera, produce carbonate that is isotopically near equilibrium (*6, 7*).

Carbon in carbonate rocks of other environments and in marine carbonates affected by certain postdepositional processes varies greatly in isotopic composition, generally in the direction of relative enrichment in C^{12}. Examples of such variable carbon are given in Table 2. The values for markedly light carbon are believed to reflect a large amount of carbon from organic matter of various kinds, all of which are invariably rich in C^{12} (*1, 8*). That bacterially decomposed petroleum was the source of the extremely light carbon in salt-dome limestones is well documented (*9, 10*). Diagenetic carbonates with light carbon commonly occur in sediments that are rich in organic matter. During some stage of diagenesis, light CO_2 derived from decomposing organic matter equilibrates with preexisting or newly forming carbonate (*11, 12*).

Our interest in diagenetic carbonates of marine formations arises from a current geochemical study of the Miocene

Table 1. Carbon isotopic composition of diagenetic dolomites and limestones in Miocene rocks of Oregon and California.

Sample No.	Locality	Geographic coordinates	Formation	Rock	δC^{13} per mil*
			Oregon samples		
1	Yaquina Bay, Lincoln County	44°38'N 124°01'W	Nye Mudstone	Dolomite bed 1	+5.4
2	Yaquina Bay, Lincoln County	44°38'N 124°01'W	Nye Mudstone	Dolomite bed 3	+10.6
			California samples		
3	Point Arena, Mendocino County	38°52'N 123°39'W	Monterey Shale	Dolomite cement of sandstone	−12.2
4	Berkeley Hills, Contra Costa County	37°52'N 122°14'W	Monterey Shale	Dolomite bed 1	+17.3
5	Berkeley Hills, Contra Costa County	37°52'N 122°14'W	Monterey Shale	Dolomite bed 5	+10.1
6	San Rafael Mts., Santa Barbara County	34°47'N 119°36'W	Monterey Shale	Limestone lens 1	+15.1
7	San Rafael Mts., Santa Barbara County	34°47'N 119°36'W	Monterey Shale	Limestone lens 2	+5.4
8	San Rafael Mts., Santa Barbara County	34°47'N 119°42'W	Monterey Shale	Dolomite bed	−12.8
9	Temblor Range, San Luis Obispo County	35°05'N 119°35'W	Monterey Shale	Dolomite bed	+19.0
10	Palos Verdes Hills, Los Angeles County	33°48'N 118°24'W	Malaga mudstone member of Monterey Shale	Dolomite bed	−16.0
11	Palos Verdes Hills, Los Angeles County	33°45'N 118°22'W	Valmonte diatomite member of Monterey Shale	Dolomite bed	−12.1
12	Palos Verdes Hills, Los Angeles County	33°45'N 118°22'W	Upper part of Altamira shale member of Monterey Shale	Dolomite bed	−5.6
13	Palos Verdes Hills, Los Angeles County	33°44'N 118°22'W	Middle part of Altamira shale member of Monterey Shale	Dolomite cement of tuff bed	−18.2

* Relative to University of Chicago Peedee belemnite carbonate standard.