IMMOBILIZED LIQUID MEMBRANES FOR CONTINUOUS CARBON DIOXIDE REMOVAL

W. J. WARD, III

FOREWORD

The research described in this report was performed under Contract No. AF-33(615)-2957 in support of Project 6373, "Equipment for Life Support in Aerospace, " and Task 637303, "Respiratory Support Equipment, " by the Research and Development Center, General Electric Company in Schenectady, New York. The research was performed between 24 May 1965 and 1 September 1966.

The program monitor for this contract is Mr. C. M. Meyer of the Biotechnology Branch, Life Support Division Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433.

The author wishes to acknowledge General Electric personnel C. P. Bean and W. L. Robb for their contributions towards conceptual and theoretical understanding of immobilized liquid films, and A. Dounoucos, C. H. Knapp, R. L. Richard, and A. F. Taussig for their contributions in developing the method of fabricating immobilized liquid films.

This technical report has been reviewed and is approved.

Wayne H. McCandless
Technical Director
Biomedical Laboratory
Aerospace Medical Research Laboratories

ABSTRACT

The objective of this program was the development of an immobilized liquid membrane for CO_2 removal from a manned spacecraft. During basic film research, water was found to be better than a polymeric material or any pure liquid for CO_2/O_2 separation. An immobilized film of water was available in the form of a porous cellulose acetate membrane fabricated at the Research and Development Center. By impregnating this membrane with a concentrated solution of $CsHCO_3/Cs_2CO_3$, and a catalyst for the hydrolysis of CO_2, CO_2 transport was facilitated and O_2 transport was decreased to obtain a CO_2/O_2 separation factor and CO_2 permeability of 4100 and $214^2 \times 10^{-9}$. A mathematical analysis of CO_2 transport was also carried out. It will now be possible to build a single-stage CO_2 removal system with minimum power, weight, and size requirements.

TABLE OF CONTENTS

LIST OF TABLES

vi

NOMENCLATURE

a_1, a_2 = integration constants; see Eq. 6

A = constant, defined by Eq. 37e

B = constant, defined by Eq. 37d

C = concentration, mols/liter

C_T = constant, defined by Eqs. 9 and 29, mols/liter

D = diffusivity, cm^2/sec

k_1 = reaction rate constant; see Eq. 2, liter/mol, sec

k_2 = reaction rate constant; see Eq. 2, sec^{-1}

k_1' = reaction rate constant; see Eq. 32, sec^{-1}

k_1'' = reaction rate constant; see Eq. 32, liter/mol, sec

k_2' = reaction rate constant; see Eq. 33, liter/mol, sec

k_2'' = reaction rate constant; see Eq. 33, sec^{-1}

K = constant, defined by Eq. 37c, cm^{-2}

K_1 = constant, defined by Eq. 37a, sec^{-1}

K_2 = constant, defined by Eq. 37b, mols/liter, sec

K' = equilibrium constant; see Eq. 17

K'' = equilibrium constant; see Eq. 2, liters/mol

K_A = equilibrium constant; see Eq. 18, mols/liter

K_w = equilibrium constant; see Eq. 20, $mols^2/liters^2$

K_B = equilibrium constant; see Eq. 19, mols/liter

L = film thickness, cm

N = flux, mols/sec, cm^2

$N_{CO_2}^T$ = total flux of CO_2, mols/sec, cm^2

Pr = permeability, $\dfrac{cc(NTP), \text{ cm thick}}{sec, cm^2, \text{ cm Hg}}$

PP_{CO_2} = partial pressure of CO_2, cm Hg

S = solubility, $\dfrac{cc \text{ gas(NTP)}}{cm^3, \text{ cm Hg}}$

x = distance into film, cm

α = separation factor, Pr_{CO_2}/Pr_{O_2}

$[\ ]$ = concentration of specie inside brackets, mols/liter

Superscripts

0 = evaluated at $x = 0$

L = evaluated at $x = L$

INTRODUCTION

In anticipation of prolonged manned space flight, many industrial and government laboratories are focusing their attention on the problems of maintaining a life-supporting environment in space. A critical problem in this area is the development of a suitable CO_2 removal system. A variety of commercial processes exist for the removal of CO_2 from gas mixtures (ref. 1). The most common of these are regenerative absorption processes using as absorbents such liquids as water, methanol, alkali carbonates, and mono- and diethanol-amines. Trace amounts of CO_2 are generally removed with caustic solutions or by a regenerative adsorption process using molecular sieves. These processes are not well suited for use in a spacecraft because one or more of the requirements is excessive: power, size, or weight.

An alternative method for gas separation involves the use of permselective membranes. If a thin (0.002 inch) membrane were available with a CO_2 permeability of

$$100 \times 10^{-9} \ \frac{\text{cc gas NTP, cm thick}^*}{\text{sec, cm}^2, \text{ cm Hg}}$$

and a CO_2/O_2 separation factor (ratio of CO_2 permeability to O_2 permeability) of at least 25, a membrane system for CO_2 removal from a spacecraft would be at least as desirable as any of the processes mentioned above.

Over the years there have been many attempts to develop membranes for various gas separations. Patents on potential processes date back to 1884, but, to date, a commercial process to separate gases by selective permeation does not exist. For CO_2/O_2 separation, the best polymeric membrane is silicone rubber, which combines a high CO_2 permeability of 300 x 10^{-9} and a relatively high CO_2/O_2 separation factor of 5.5. However, this separation factor is inadequate for a practical CO_2 removal system for a spacecraft. Several years ago, W. L. Robb and D. L. Reinhard of the Research and Development Center, General Electric Company, considered liquids as potential membrane materials. Certain liquids possess very desirable permeation characteristics, such as water which has a CO_2/O_2 separation factor of 22 and a CO_2 permeability of 210 x 10^{-9}.

The objective of this contract was twofold:

Develop a prototype of an immobilized liquid membrane system for CO_2 removal from a manned spacecraft.

Develop an immobilized liquid membrane approximately 1 mil thick having a separation factor of at least 20.

---

*These units for permeability will be used throughout this report.

The objectives of Phase I were:

to select the optimum liquid to be used in the film.

to devise a method of fabricating an immobilized film of this liquid on the order of 1 mil thick.

The permeation characteristics of the membranes finally developed exceed the specifications set forth in the original proposal.

Section II

PERMEATION IN PURE LIQUIDS

When the diffusion coefficient D of a permeant is independent of concentration and time, and when the solubility S follows Henry's law, the following relation is obtained

$$Pr = DS \qquad (1)$$

This equation holds well enough to serve as a guide in selecting suitable liquids for the gas separation desired. Since the diffusion coefficient is of the order of 10^{-5} cm^2/sec for most solutes in most liquids, the primary concern is to find liquids with high CO_2 solubilities and low oxygen solubilities.

Extensive data on CO_2 and O_2 solubilities in liquids are available (refs. 2 and 3). Water is an obvious choice for separating these two gases since, at 25 C, it has a CO_2 solubility 27 times greater than O_2. The permeabilities of CO_2 and O_2 in water and in diethylene glycol were previously measured and these measurements were repeated for this present study with results presented in table I. A large number of organic liquids have CO_2 solubilities higher than water, however, all of the organic liquids considered in this work have relatively high O_2 solubilities and would not give separation factors higher than water. In a practical system for CO_2/O_2 separation, a low vapor pressure nontoxic liquid for the film is desirable and may override in importance a somewhat lower separation factor. On the basis of high CO_2 solubility (at least two times higher than water), low vapor pressure (less than 1 mm Hg), and negligible toxicity, d-carvone and eugenol were selected for permeability measurements. Results are presented in table I.

Table I

EXPERIMENTAL RESULTS FOR THE PERMEABILITY OF CO_2 AND O_2 THROUGH LIQUID FILMS

Liquid	$Pr_{CO_2} \times 10^9$	$Pr_{O_2} \times 10^9$	$\alpha = Pr_{CO_2}/Pr_{O_2}$
Water	630	14.5	44
Diethylene glycol	55.8	2.6	21
d-Carvone	526	41.8	13
Eugenol	330	25	14

A sketch of the apparatus and an outline of the procedure used to obtain the data in table I are presented in Appendix I.

Based on the known solubility of CO_2 and O_2 in water, a film of water has a CO_2 permeability of 210×10^{-9} and a CO_2/O_2 separation factor of 22. The experimental results were not in agreement with calculated values. This is explained by the fact that during mass transfer, convection currents were

3

established in the liquid film which resulted in an apparent permeability significantly higher than the true value. To check this conclusion, CO_2 and O_2 permeabilities were measured in water films containing 1 percent gelatin to eliminate convection. The CO_2 and O_2 permeabilities were 280×10^{-9} and 10×10^{-9}, respectively, which are in reasonable agreement with the calculated values.

The method used to obtain the results given in table I is unsatisfactory for obtaining accurate permeability data. However, it can be concluded from this work that there is no pure liquid other than water which would give a substantially higher CO_2 permeability and CO_2/O_2 separation factor.

Section III

IMMOBILIZATION OF AN AQUEOUS FILM

A method was sought to immobilize a film of water when an aqueous film was found to be at least as desirable as any other liquid for CO_2/O_2 separation. In 1960, Loeb and Sourirajan (ref. 4) produced a modified cellulose diacetate membrane for use in a reverse osmosis process for desalination. A similar membrane has been produced in the Research and Development Center. The structure of the membrane is shown in figure 1. The standard membrane thickness was 2.6 to 2.8 mils although this could be varied over a wide range.

ULTRA THIN DENSE SKIN OF CELLULOSE ACETATE

2.7 MILS

POROUS CELLULOSE ACETATE, 60(wt)% WATER
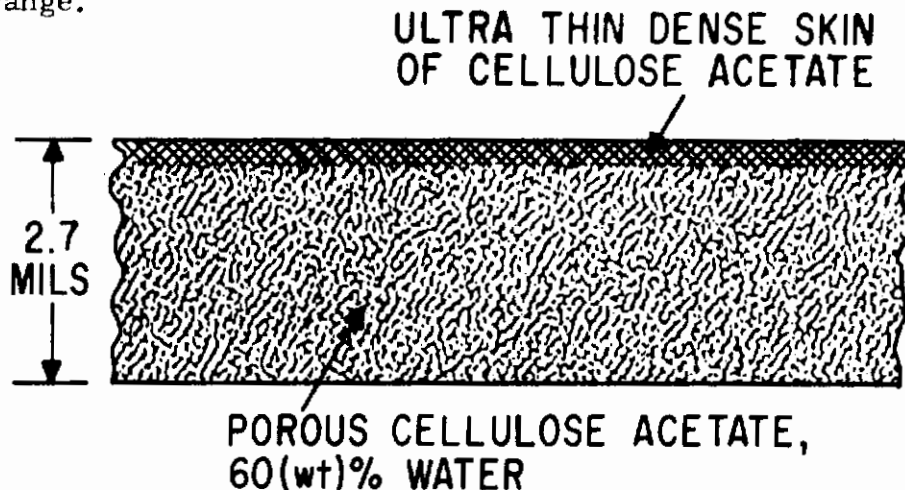
Figure 1. Structure of porous cellulose acetate membrane
used as a liquid membrane.

The fact that most of the film contained 60 percent water suggested that it might have the permeation characteristics of water. The resistance of the ultrathin dense skin to the permeation of gases should be negligible compared to the total resistance of the film. Using the apparatus described in Appendix I, the permeabilities of CO_2 and O_2 were measured in a large number of Loeb-type films containing pure water. The average of the results obtained is:

$$Pr_{CO_2} = 40 \times 10^{-9}$$

$$Pr_{O_2} = 2 \times 10^{-9}$$

$$CO_2/O_2 \text{ separation factor } = \alpha = 20$$

The values of the permeabilities varied as much as $\pm$ 20 percent from one film to another, but the separation factor was reproducible. The results indicate that the cellulose acetate film did have permeability characteristics similar to those of water, and that the only effect of the polymer was to lower the values of the diffusivities.. The wide variation in the values of the permeability from one film to another was due to variation ($\pm$ 4 percent) in the water content of the films used.

5

The Loeb-type cellulose acetate film was attractive for the present application. It was tough, contained no pinholes, and could be made as thin as 1 mil. The major liability of the film was that if it dried out, it cracked and broke apart. Thus, if the film were impregnated with pure water, it always had to be in contact with gas saturated with water vapor. To make permeability measurements on the modified cellulose acetate film, it was useful to back the film on the low-pressure side with a very thin (1-mil) silicone rubber membrane. This served to minimize water transport across the film. The effect of the silicone rubber on the CO_2 and O_2 permeabilities of the cellulose acetate-silicone rubber composite was negligible. It will be desirable to use the silicone rubber backing in any practical system using the cellulose acetate film.

Another method to control drying of the cellulose acetate was to impregnate the film with a salt solution and thus lower the equilibrium partial pressure of water over the film. To test the effect of an inert salt on gas permeabilities, a modified cellulose acetate film was soaked in a 20 percent potassium chloride solution for 1 day. The CO_2 and O_2 permeabilities in this film were measured and found to be 32×10^{-9} and 1×10^{-9}, respectively. These values were reproducible over a three-day period, indicating that the drying with resulting stress cracking, which frequently occurred in films containing pure water, was eliminated. The proper electrolytes not only alleviated the drying problem, but had a profound effect on gas permeabilities.

FACILITATED TRANSPORT

PRINCIPLE OF FACILITATED TRANSPORT

Assume that species A is a gas and that B and AB are nonvolatile molecular or ionic species present in a liquid film. Let A react with B according to the reaction $A + B \rightleftharpoons AB$. If a concentration difference in A is maintained across the film, a concentration difference in AB is established which is in the same direction as the A concentration difference. A concentration difference in B is also established which is in the opposite direction to the A concentration difference. As a result of the concentration differences, there is a net transport of A and AB in the same direction across the film, and a net transport of B equal in magnitude and opposite in direction to the transport of AB. Since the total flux of A across the film is equal to the flux of A plus AB at any point in the film, the flux of A is facilitated or augmented as a result of the presence of the nonvolatile species B and AB. In effect, a shuttle for A has been established and under the proper conditions, the flux of A can be increased many orders of magnitude by this mechanism. Thus, a high degree of separation between A and nonreacting gases can be attained.

The following analysis of facilitated transport illustrates the extent to which the total transport of A can be increased by a nonvolatile carrier B. This treatment is similar to that of Olander (ref. 5), who analytically studied a system which was physically unrelated but mathematically analogous to the present one. For the sake of illustration, the reaction to be considered is

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \tag{2}$$

where k_1 and k_2 are the rate constants of the forward and reverse reactions. Since the liquid film is a multicomponent system, a completely rigorous treatment of transport across the film would require the use of multicomponent diffusion coefficients. However, the solute concentrations in the film will be assumed to be sufficiently dilute that Fick's law is applicable. Diffusion coefficients are considered to be those of the binary system consisting of the particular species and the solvent. Differential mass balances on A and AB at any point in the film are:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A C_B + k_2 C_{AB} \tag{3}$$

$$\frac{\partial C_{AB}}{\partial t} = D_{AB} \frac{\partial^2 C_{AB}}{\partial x^2} + k_1 C_A C_B - k_2 C_{AB} \tag{4}$$

7

where x is the distance into the film with the surfaces of the film being at $x = 0$ and $x = L$. The concentration of A at $x = 0(C^o_A)$ and at $x = L(C^L_A)$ was assumed to be known. The left-hand sides of Equations 3 and 4 are zero since the system is assumed to be at steady state. Adding Equations 3 and 4 gives

$$D_A \frac{\partial^2 C_A}{\partial x^2} + D_{AB} \frac{\partial^2 C_{AB}}{\partial x^2} = 0 \tag{5}$$

The solution to Equation 5 is

$$D_A C_A + D_{AB} C_{AB} = a_1 x + a_2 \tag{6}$$

where a_1 and a_2 are constants. The total flux if A is

$$N^T_A = D_A \frac{\partial C_A}{\partial x} + D_{AB} \frac{\partial C_{AB}}{\partial x} \tag{7}$$

Equation 7 is valid at all points within the film and from Equation 6

$$N^T_A = a_1 \tag{8}$$

With this type of analysis, the only way to evaluate N^T_A in terms of C^o_A and C^L_A is to assume that the reacting species are present in equilibrium concentrations at all points in the film. With this assumption and the fact that

$$C_{AB} + C_B = C_T \tag{9}$$

where C_T is a constant, the expression for the total flux of A is

$$N^T_A = \frac{D_A}{L} \left(C^o_A - C^L_A \right) + \frac{D_{AB} K'' C_T}{L(1 + K'' C^o_A)(1 + K'' C^L_A)} \left(C^o_A - C^L_A \right) \tag{10}$$

where K'' is the equilibrium constant of the reaction $A + B \rightleftarrows AB$. The first term on the right-hand side of Equation 10 is the flux of dissolved A across the film. The second term on the right-hand side of Equation 10 is the flux of AB across the film, and it is this term that represents the facilitated transport of A. The flux of AB is a function of K'', and from Equation 10 the maximum flux of AB can be shown to occur when

$$K'' = \frac{1}{C^o_A C^L_A} \tag{11}$$

If D_A is equal to D_{AB}, if C^L_A is zero, and if K'' is sufficiently large that

$$1 + K'' C^o_A \approx K'' C^o_A \tag{12}$$

8

then the flux of AB is C_T/C_A^o times the flux of dissolved A. C_T can be made thousands of times larger than C_A^o and thus the total flux of A can be increased many orders of magnitude as a result of facilitated transport.

AN EXAMPLE OF FACILITATED TRANSPORT

There are several references in the literature to diffusion in liquids mediated by moving carriers (ref. 6). An example of facilitated transport, which is clearly diffusion mediated by moving carriers, was discovered in 1959 by Scholander (ref. 7), and Wittenberg, (ref. 8). Both investigators, working independently, found that various hemoglobins in water solutions increased the steady-state transport of oxygen through that solution. As a result of this work, in the last 6 years, a considerable amount of experimental and theoretical work has been done on steady-state oxygen diffusion in aqueous solutions containing proteins that react reversibly with oxygen (refs. 9-15). Most of the experimental work was done by measuring the steady-state rate of transport of oxygen across a thin film of aqueous hemoglobin solution. This "liquid membrane," first used by Scholander (ref. 7), was prepared by impregnating a 0.15-mm-thick millipore membrane of 80 percent porosity with the hemoglobin solution.

Oxygen reacts reversibly with hemoglobin in four steps (ref. 16). Based on this, there have been several conflicting theories advanced to explain the experimental fact that hemoglobin water solutions increase the steady-state transport of oxygen through that solution. The mechanism of facilitated oxygen transport is the same as that outlined above where

$$A = \text{oxygen}$$
$$B = \text{hemoglobin}$$
$$AB = \text{oxyhemoglobin}$$

In the mathematical treatments of facilitated oxygen transport, the reaction between oxygen and hemoglobin was

$$\text{Hb} + \text{O}_2 \rightleftarrows \text{HbO}_2 \tag{13}$$

Wyman (ref. 12) was the first to set up the differential equation for the total oxygen transport in which the rate of the above reaction was allowed to be slow. However, he stated that "No analytical or numerical solution of the equation was yet available." Thus he assumed chemical equilibrium at all points in the film and derived the oxygen flux equation already obtained (refs. 9 and 10). The agreement between the experimental data of Wittenberg (ref. 11), and the calculated result of Wyman (ref. 12) for the total oxygen flux was satisfactory. In the most recent paper on facilitated transport, LaForce (ref. 14) presented an analytical analysis of steady-state diffusion in the carbon monoxide-oxygen-hemoglobin system. That paper is of particular importance because for the first time the differential equations governing steady-state diffusion in this system were solved (numerically) without assuming chemical equilibrium between the reacting species.

9

FACILITATED TRANSPORT OF CO$_2$

INTRODUCTION

It would be desirable in the problem of CO$_2$/O$_2$ separation if the transport of CO$_2$ across an aqueous membrane could be facilitated. The chemistry and kinetics of the hydration of CO$_2$ are not yet completely understood although Chemical Engineering literature is filled with references on the absorption and transport of CO$_2$ in aqueous solutions (ref. 17). In principle, CO$_2$ transport across an aqueous film could be facilitated by establishing a concentration gradient in HCO$_3^-$ in the same direction as the CO$_2$ gradient. The HCO$_3^-$ would act as CO$_2$ carrier because on the high-pressure side of the film (high partial pressure of CO$_2$), CO$_2$ would react to form HCO$_3^-$, the HCO$_3^-$ would migrate across the film because of its concentration gradient, and, at the low-pressure side, the HCO$_3^-$ would decompose to produce CO$_2$.

In order to have significant facilitated CO$_2$ transport, there must be a significant concentration of HCO$_3^-$ in the film. To establish this a bicarbonate salt or a base could be added to the film. If a base were added, HCO$_3^-$ would be produced upon the absorption of CO$_2$ in the film. A simple relationship exists among the concentrations of CO$_2$, HCO$_3^-$, and CO$_3^=$ which is derived as follows. The species present in an aqueous solution in which CO$_2$ is absorbed are H$_2$O, H$^+$, OH$^-$, CO$_2$, H$_2$CO$_3$, HCO$_3^-$, CO$_3^=$. Assume that the following reactions occur:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{14}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{15}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \tag{16}$$

Equilibrium constants for Equations 14 through 16 are known (ref. 18). Equilibrium may exist among the reacting species throughout the film. Thus, whether or not the above reactions occur is immaterial since they can be used to calculate the concentration of all the species present at any point in the film. The concentration of CO$_3^=$ is calculated by combining Equations 14, 15, and 16 and the known equilibrium constants to give (for dilute solutions)

$$[CO_3^=] = 1.3 \times 10^{-4} \left(\frac{[HCO_3]^2}{[CO_2]} \right) \tag{17}$$

To maintain electrical neutrality with a concentration difference in HCO$_3^-$ across the film there must be a concentration difference in some other charged species across the film. In the discussions under this section, a very weak base (BOH) is present in the film and the concentration gradient in HCO$_3^-$ is balanced by a gradient in B$^+$. To simplify the analysis of this case,
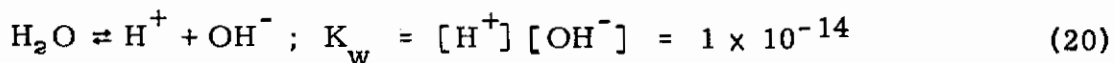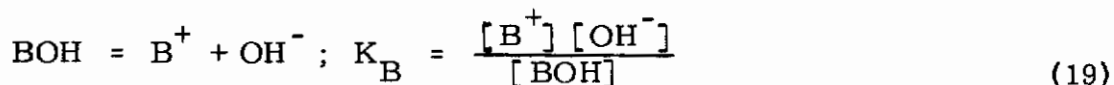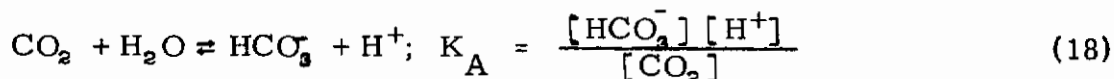
10

conditions are such that the concentration of $CO_3^=$ is negligible compared to the concentration of HCO_3^-. In the discussion later in this section, a HCO_3^- salt is added to the film, the $CO_3^=$ concentration is the same order of magnitude as the HCO_3^- concentration, and the HCO_3^- concentration gradient is balanced by a concentration gradient in $CO_3^=$.

FACILITATED TRANSPORT OF CO_2 IN AQUEOUS SOLUTIONS OF BASES

Analytical

A base, BOH, is added to an aqueous film in order to establish a significant concentration of HCO_3^-. The concentration of HCO_3^- and pressure of CO_2 are such that the concentration of $CO_3^=$ is never more than 10 percent of the concentration of HCO_3^-. The concentration of H_2CO_3 is also negligible (ref. 19). The following calculations show under what conditions a concentration difference in HCO_3^- across the film can be established. The reactions to be considered are:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+; \quad K_A = \frac{[HCO_3^-][H^+]}{[CO_2]} \tag{18}$$

$$BOH = B^+ + OH^-; \quad K_B = \frac{[B^+][OH^-]}{[BOH]} \tag{19}$$

$$H_2O \rightleftarrows H^+ + OH^-; \quad K_w = [H^+][OH^-] = 1 \times 10^{-14} \tag{20}$$

The condition of electrical neutrality is

$$[HCO_3^-] + [OH^-] = [B^+] + [H^+] . \tag{21}$$

Combining Equations 18 through 21 gives:

$$[HCO_3^-] + \frac{K_w |HCO_3|}{K_A |CO_2|} = \frac{K_A |CO_2|}{|HCO_3|} + \frac{K_B |BOH*|}{\dfrac{K_w |HCO_3|}{K_A |CO_2|} + K_B} \tag{22}$$

where [BOH*] = moles/liter of base added to the water. Equation 22 is an implicit expression for the concentration of HCO_3^- in terms of known quantities and K_B (to which a series of values will be assigned). Using this equation, table II was constructed in which the value of the concentration of HCO_3^- was calculated for various values of $C_{CO_2}^\circ$, $C_{CO_2}^\dagger$, and a series of values of K_B. When the concentration of $CO_3^=$ is negligible, then only the addition of very weak bases (K_B 10^{-6}) results in any significant concentration difference in HCO_3^- across the film, and thus any significant facilitated transport.

Table II

BICARBONATE CONCENTRATION IN TERMS OF KNOWN SYSTEM REQUIREMENTS

Case	K_B	Upstream Side of Film			$C_{HCO_3^-}$ Downstream for:		
		(BOH*)	$C^0_{CO_2}$	$C^0_{HCO_3^-}$	$C^L_{CO_2} = 0.016$	$C^L_{CO_2} = 3.3 \times 10^{-4}$	$C^L_{CO_2} = 1.6 \times 10^{-4}$
1	1.0	0.033	0.033	0.033	0.033	0.033	0.033
2	2.2×10^{-6}	.033	.033	.033	.033	.020	.016
3	2.2×10^{-7}	.034	.033	.033	.029	.0088	.0063
4	2.2×10^{-8}	.066	.033	.033	.026	.0045	.0031
5	2.2×10^{-9}	.361	.033	.033	.023	.0034	.0024
6	2.2×10^{-6}	3.3×10^{-4}	3.3×10^{-4}	3.3×10^{-4}			3.3×10^{-4}
7	2.2×10^{-7}	3.6×10^{-4}	3.3×10^{-4}	3.3×10^{-4}			3.0×10^{-4}
8	2.2×10^{-8}	6.6×10^{-4}	3.3×10^{-4}	3.3×10^{-4}			2.5×10^{-4}
9	2.2×10^{-9}	3.6×10^{-3}	3.3×10^{-4}	3.3×10^{-4}			2.3×10^{-4}
10	2.2×10^{-10}	3.6×10^{-2}	3.3×10^{-4}	3.3×10^{-4}			2.5×10^{-4}

NOTES: Units of concentration are moles/liter.

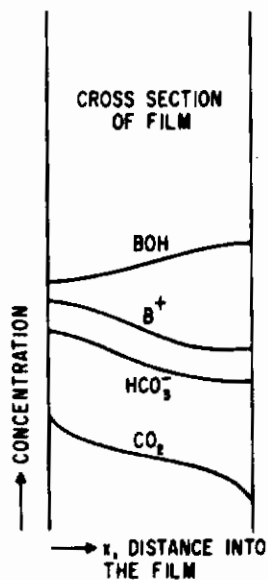$C_{CO_2} = 0.033$ is the concentration of CO_2 in water at 25°C in equilibrium with CO_2 gas at 1 atm.

Figure 2. Concentration profiles in an aqueous film containing a weak base, BOH.

In all cases considered in table II, the concentration of H^+ and OH^- are small compared to the HCO_3^- concentration. Thus, in those cases where there is a HCO_3^- concentration gradient there is also an equal concentration gradient in B^+. A schematic diagram illustrating the concentration profiles of the species present is shown in figure 2. Note in figure 2 that the concentration gradient of all nonvolatile species is zero at the surfaces of the film. This must be the case in order that the flux of the nonvolatile species be zero at the surface.

Calculation of the effect of the base, BOH, on the total flux of CO_2 across a liquid membrane containing the base is straightforward if the reacting species are assumed to be present at equilibrium concentrations at all points in the film. The total flux of CO_2 across the film is equal to the total flux of carbon. Assuming Fick's law applies, the total flux of CO_2 is as shown in Equation 23.

$$N_{CO_2}^T = -D_{CO_2}\left(\frac{\partial C_{CO_2}}{\partial x}\right) - D_{HCO_3^-}\left(\frac{\partial C_{HCO_3^-}}{\partial x}\right) \tag{23}$$

Integrating over the thickness of the film gives

$$N_{CO_2} = \frac{D_{CO_2}(C_{CO_2}^o - C_{CO_2}^L)}{L} + \frac{D_{HCO_3^-}(C_{HCO_3^-}^o - C_{HCO_3^-}^L)}{L} \tag{24}$$

Making the reasonable assumption that the diffusivity of HCO_3^- is approximately the same as the diffusivity of CO_2, one can then immediately calculate the effect of the base BOH on the total CO_2 flux using table II. For example, in case 10 of table II one would expect the effect of the base to be to double the CO_2 flux across the film.

Experimental

As a result of this analysis, the permeability of CO_2 in aqueous films to which several different bases were added was measured. The results are presented in table III. The apparatus and procedure used to obtain these data are discussed in Appendix I. Unfortunately, because the aqueous films were not immobilized in these measurements, convection currents were undoubtedly present during the transport of CO_2. Thus, only a qualitative comparison of these data and the analysis in table III is feasible.

The presence of dilute NaOH had no effect on the permeability of CO_2. The analysis in table III is applicable to monobasic materials and thus should apply to the β-picoline and pyridine results. The concentration of β-picoline used was such that its presence should have doubled the permeability of CO_2. Under the conditions of the particular experiment under consideration, the convective transport of CO_2 was roughly two times the diffusive transport. Addition of β-picoline to the film should double the diffusive transport, but it should not affect the convective transport. Thus, the 50 percent increase in CO_2 permeability observed for β-picoline is not unreasonable. A similar comparison is possible with the pyridine results. At a concentration of 0.5 N

the diffusive flux of CO_2 should be doubled. Thus, because of convection currents in the film, the 60 percent increase that was observed is reasonable.

Table III

EFFECT OF BASES ON THE PERMEABILITY OF CO_2

Base	K_B	Base Added to Film (mol/l)	Ratio Pr_{CO_2} in Aqueous Solution of Base to Pr_{CO_2} in Pure Water†
NaOH		0.03	1.0
p-Phenylene-diamine	$K_1 = 1.1 \times 10^{-8}$ $K_2 = 3.5 \times 10^{-12}$	.056	1.2
Piperazine	$K_1 = 6.4 \times 10^{-5}$ $K_2 = 3.7 \times 10^{-9}$	.03	1.2
β-Picoline	1×10^{-8}	.103	1.5
Pyridine	1.71×10^{-9}	.0025	1.2
		.10	1.3
		.25	1.5
		.50	1.6
		1.25	1.7

†To obtain a meaningful comparison here, the value of the Pr_{CO_2} used is the experimental value of 630×10^{-9} (see table I), even though this value is high due to convection.

The effect of the dibasic materials studied, piperazine and p-phenylene-diamine, on the CO_2 permeability is rather complex and the above analysis is not applicable. It was decided not to carry out the laborious, although straightforward, procedure to predict the HCO_3^- concentration in terms of known system requirements.

The results of the work on weak bases were encouraging since they showed the diffusive flux of CO_2 could at least be doubled. This implied that an immobilized aqueous film, containing a weak base, would have a CO_2/O_2 separation factor of approximately 50. The major liability of all of the bases tested, and many like them, is that they are toxic. No additional work was done with weak bases because the preliminary work carried out pointed the way to a method of obtaining much higher separation factors.

14

FACILITATED TRANSPORT OF CO_2 IN AQUEOUS $HCO_3^-/CO_3^=$ SOLUTIONS

Introduction

The steady-state transport of CO_2 across an aqueous film containing significant concentrations of HCO_3^- and $CO_3^=$ is considered in this section. From Equation 17 for an appreciable concentration of $CO_3^=$ to be present, the HCO_3^- concentration must clearly be sufficiently high and the CO_2 concentration sufficiently low. The distribution of HCO_3^- and $CO_3^=$ as a function of the partial pressure of CO_2 in equilibrium with the solution are shown for two specific cases in figures 3 and 4. In figure 3, for a $KHCO_3/K_2CO_3$ solution, the concentration of K^+ is 2N. The equilibrium relation used in figure 3 was experimentally determined by Walker et al. (ref. 20). In figure 4, for a $CsHCO_3/CsCO_3$ solution, the concentration of Cs^+ is 6.44N. The equilibrium constant for dilute solutions was used because no experimental data are available for this system. These two examples were selected because the concentration of saturated solutions of $KHCO_3$ and $CsHCO_3$ are
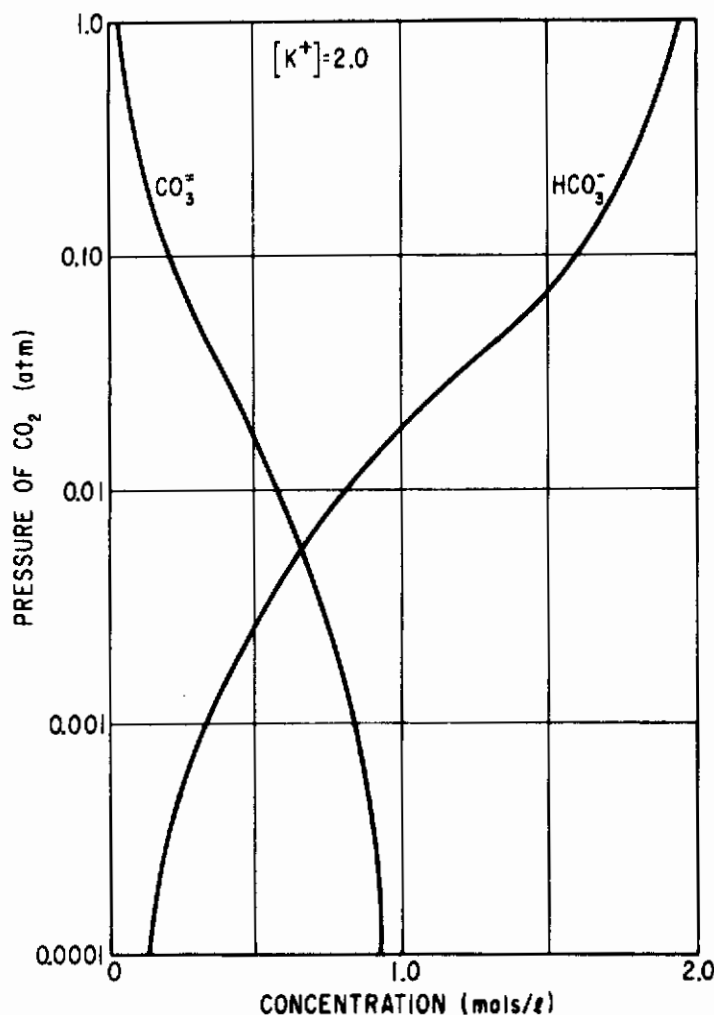

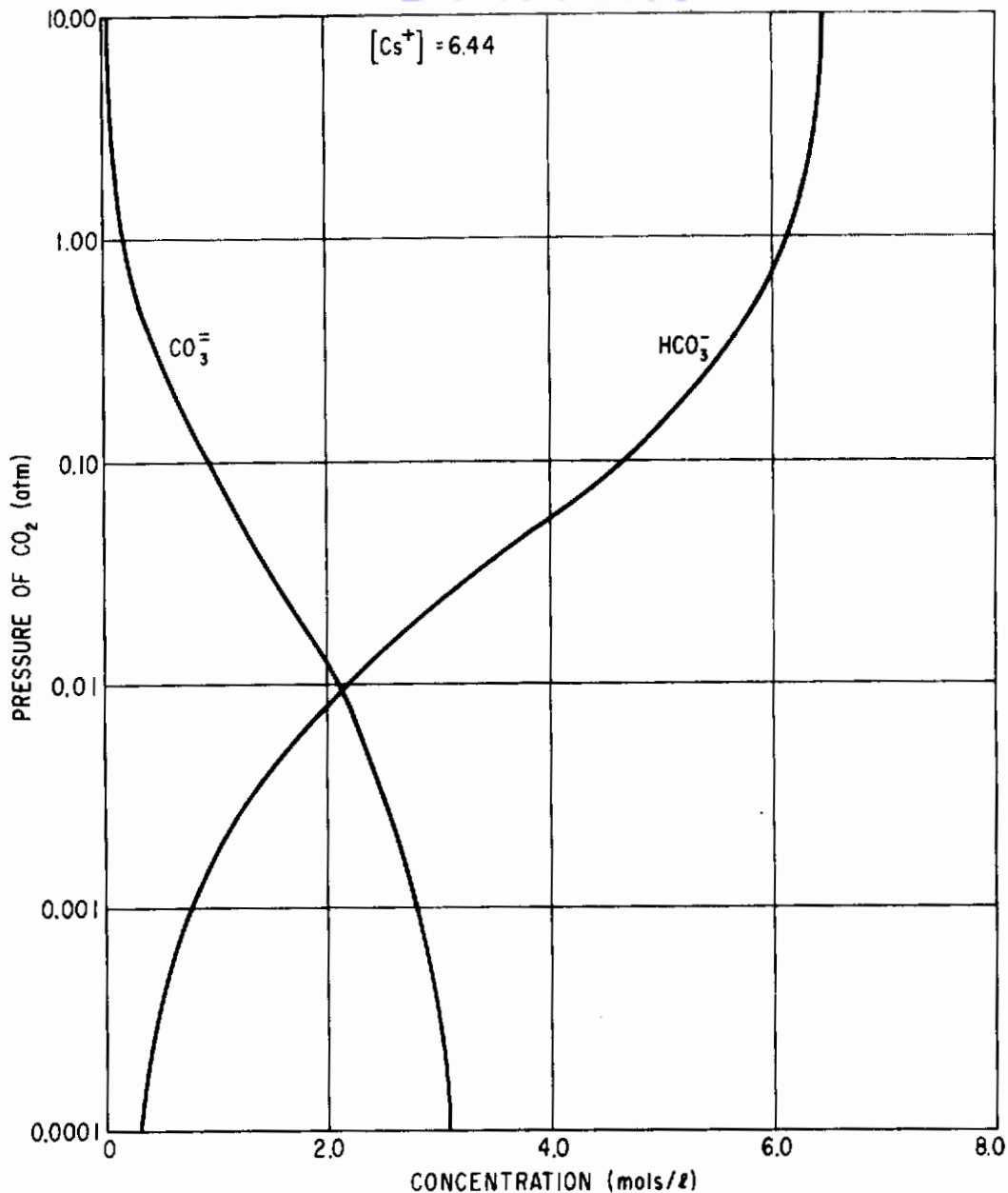Figure 3. Distribution of HCO_3^- and $CO_3^=$ as a function of the pressure of CO_2, $[K^+]$ = 2.0

15

Figure 4. Distribution of HCO_3^- and $CO_3^=$ as a function of the pressure of CO_2, $[Cs^+] = 6.44$.

2N and 6.44N respectively. The figures illustrate that in the proper range of concentrations, an aqueous film having a concentration difference in CO_2 across it may have very large and opposing concentration differences in HCO_3^- and $CO_3^=$ also across it. A concentration difference in HCO_3^- across the film is desired to promote facilitated transport of CO_2. The presence of a concentration difference in $CO_3^=$ in the opposite direction permits the concentration difference in HCO_3^- since it satisfies the condition of electrical neutrality.

Consider quantitatively the effect of large concentrations of HCO_3^- and $CO_3^=$ on the total CO_2 flux in an aqueous film across which there is a concen-

16

tration difference in CO_2. The total flux of CO_2 is equal to the total flux of carbon at any point in the film. Assuming that Fick's law applies

$$N_{CO_2}^T = - \left(D_{CO_2}\right) \frac{\partial C_{CO_2}}{\partial x} - \left(D_{HCO_3^-}\right) \frac{\partial C_{HCO_3^-}}{\partial x} - \left(D_{CO_3^=}\right) \frac{\partial C_{CO_3^=}}{\partial x} \quad (25)$$

Neglecting the effect of very small concentration of H^+ and OH^-, the condition of electrical neutrality requires that

$$\left(\frac{D_{HCO_3^-}}{2}\right) \frac{\partial C_{HCO_3^-}}{\partial x} = \left(-D_{CO_3^=}\right) \frac{\partial C_{CO_3^=}}{\partial x} \quad (26)$$

Substituting Equation 26 into 25 and integrating across the film gives

$$N_{CO_2}^T = \frac{D_{CO_2}^\circ \left(C_{CO_2}^\circ - C_{CO_2}^L\right)}{L} + \frac{D_{HCO_3^-}}{2} \frac{\left(C_{HCO_3^-}^\circ - C_{HCO_3^-}^L\right)}{L} \quad (27)$$

Equation 27 is useful if one knows $C_{HCO_3^-}^\circ$ and $C_{HCO_3^-}^L$ in terms of $C_{CO_2}^\circ$ and $C_{CO_2}^L$ (the latter terms are assumed to be known). If it is assumed that all reacting species in the film are present in equilibrium concentrations, then the surface concentration of HCO_3^- is known. Making this assumption and writing the concentration of HCO_3^- in terms of the concentration of CO_2, the total CO_2 flux is shown in Equation 28.

$$N_{CO_2}^T = \frac{D_{CO_2} \left(C_{CO_2}^\circ - C_{CO_2}^L\right)}{L} + \frac{D_{HCO_3^-}}{8K'L} \left[\left(C_{CO_2}^\circ + 16K'C_T C_{CO_2}\right)^{1/2} \right. \quad (28)$$

$$\left. - \left(C_{CO_2}^{L^2} + 16K'C_T C_{CO_2}^L\right)^{1/2} - \left(C_{CO_2}^\circ - C_{CO_2}^L\right) \right]$$

where K' is the numerical constant in Equation 17 and where C_T is a constant and is defined by

$$C_T = C_{HCO_3^-} + 2C_{CO_3^=} \quad (29)$$

The second term of Equation 28 represents the facilitated transport of CO_2. Under the proper conditions this term may be orders of magnitude larger than the first term. In the next section, Equation 28 is compared with experimental results.

Experimental Results

The permeability of CO_2 and O_2 in immobilized liquid films containing $HCO_3^-/CO_3^=$ solutions have been measured. The film which was used for all

17

of these measurements was the porous cellulose acetate film described in Section 3. Films of $HCO_3^-/CO_3^=$ solutions were made by soaking the cellulose acetate membrane in a HCO_3^- solution for at least 1 day. The thickness of all of the films used was 2.6 to 2.8 mils unless otherwise noted.

To obtain meaningful data from which to calculate the CO_2/O_2 separation factor, it was necessary to measure CO_2 and O_2 permeabilities simultaneously. Thus, a mixture of CO_2 and O_2 was passed over the film, the rate at which the product gas passed through the film was measured, and the relative amount of CO_2 and O_2 in the product gas was determined by an appropriate sampling procedure followed by analysis on a mass spectrometer. The CO_2/O_2 feed gas was always preconditioned with water vapor such that the partial pressure of water in the gas was in equilibrium with the water in the film.

Many of the preliminary data were obtained on an apparatus in which the operation was batchwise. The system was identical to that described in Appendix I except that a sampling bulb was affixed to region (A) by means of a ground glass joint. A mixture of moist CO_2 and O_2 was circulated continuously over the film, and gas passing through the film was accumulated at a measured rate on the low-pressure side. After an interval of time the accumulated gas was expanded into an empty sample bulb. The gas in the sample bulb was then expanded into a mass spectrometer where the relative amount of CO_2 and O_2 was determined. Useful data were obtained with this procedure, but since the partial pressure of CO_2 on the low-pressure side was always changing, the permeability of CO_2 was always changing (see Equation 28). Also, the rate at which gas permeated the film could be measured only very approximately. Thus, an apparatus was constructed in which steady-state operation could be maintained indefinitely and the product gas could be sampled without disturbing conditions near the film. With this apparatus and the mass spectrometer analysis the following could be accomplished.

1. The pressure on the low-pressure side of the film could be varied over a wide range and the partial pressure of each gas could be determined accurately.

2. The values of the permeabilities of CO_2 and O_2 could be measured accurately as a function of the partial pressure of CO_2 and O_2 on each side of the film.

For details of the apparatus and operation see Appendix II.

A large amount of data were collected on the permeation of CO_2 and O_2 in $HCO_3^-/CO_3^=$ films, but much of it was preliminary in nature and pointed the way to methods for further improvement in separation factor. Thus, in the following discussion not all of the data that were obtained are reviewed.

Using the equipment for batchwise permeability measurements, the CO_2/O_2 separation factor in porous cellulose acetate films impregnated with a solution which was originally 2N $KHCO_3$ was measured. In the presence of CO_2 the solution in the film became a mixture of HCO_3^- and $CO_3^=$. The

18

feed gas contained 4.5 percent CO_2. The partial pressure of CO_2 plus O_2 on the low-pressure side went from zero to 0.2 cm Hg. The average of at least four different measurements on six different films gave a separation factor of 50. With this equipment the absolute permeabilities of CO_2 and O_2 could only be determined very approximately. The CO_2 permeability was not significantly different from the value of 40×10^{-9} reported in Section 3 for a cellulose acetate film impregnated with pure water. It is of interest to compare this result with pure water. Comparison of this result with that predicted by Equation 28 is interesting. The following constants inserted into Equation 28 are representative of the experimental conditions.

$$PP_{CO_2}^{\circ} = 3.4 \text{ cm Hg}$$

$$PP_{CO_2}^{L} = 0.2 \text{ cm Hg}$$

$$K' = 2.5 \times 10^{-4} \quad (20) \text{ [defined by Equation 17]}$$

$$C_T = 2.0 \text{ mols/liter}$$

$$D_{CO_2} = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$D_{HCO_3^-} = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

Solubility of CO_2 in film = 0.03 mol/liter at 1 atm CO_2. Inserting these values into Equation 28 the CO_2 flux is 2.1×10^{-7} mols/sec-cm^2. This corresponds to a CO_2 permeability of $11,600 \times 10^{-9}$. The very wide discrepancy between the experimental and predicted values for the CO_2 permeability is discussed below.

The results with $KHCO_3$ were sufficiently encouraging to go to higher salt concentrations. $CsHCO_3$ was used since it is the most soluble alkali HCO_3^-. Using equipment described in Appendix II, the CO_2 and O_2 permeabilities of a large number of cellulose acetate films impregnated with a saturated solution of $CsHCO_3$ were measured. The results were reproducible for a given film and among films cut from the same large sheet, but among films from different sheets there was a rather large spread in the data. It was difficult to cast films with exactly reproducible properties, and it was because the films had a somewhat variable porosity that the data were scattered. A consistent and representative set of data was obtained using small samples of film cut from a single large sheet. Measurements were made on three such samples impregnated with saturated $CsHCO_3$ solution. The feed gas was at 70 percent relative humidity (which is in equilibrium with the water in the film) and contained 4.5 percent CO_2 in O_2 at 1 atm. The partial pressure of CO_2 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 of the CO_2 permeability and separation factor, and the average of all the results obtained is

19

$$Pr_{CO_2} = 75 \times 10^{-9} \pm 20 \text{ percent}$$

$$Pr_{O_2} = 0.054 \times 10^{-9} \pm 20 \text{ percent}$$

$$\alpha = 1400 \pm 15 \text{ percent}$$

Compared with the same values for pure water in cellulose acetate (see Section 3), the effect of the $CsHCO_3$ was to raise the permeability of CO_2 almost a factor of two and to lower the permeability of O_2 almost a factor of 40. For comparison of these results with Equation 28, the following constants are applicable:

$$PP_{CO_2}^0 = 3.4 \text{ cm Hg}$$

$$K' = 1.3 \times 10^{-4}$$

$$C_T = 6.44 \text{ mols/liter}$$

$$D_{CO_2} = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$D_{HCO_3^-} = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

Solubility of CO_2 in film $= 0.03$ mol/liter at 1 atm

Inserting these values and $PP_{CO_2}^L = 0.4$ cm Hg into Equation 28, the CO_2 flux is 4.9×10^{-7} mol/sec-cm^2 which corresponds to a CO_2 permeability of $29,000 \times 10^{-9}$. Inserting the constants above and $PP_{CO_2}^L = 2.1$ cm Hg into Equation 28, the CO_2 flux is 1.4×10^{-7} mols/sec-cm^2 which corresponds to a CO_2 permeability of $18,000 \times 10^{-9}$.

These experimental results were very encouraging since a CO_2/O_2 separation factor was attained which was vastly higher than had ever been attained previously. However, the question that arises is why the CO_2 permeabilities obtained in the two cases above are hundreds of times lower than those predicted by Equation 28. One explanation is that the value of $D_{HCO_3^-}$ used is much too high. There is no reason to suspect that the values of $D_{HCO_3^-}$ and D_{CO_2} differ by several orders of magnitude. Furthermore, the value of $D_{HCO_3^-}$ cannot be readily determined, so the hypothesis is not a useful one. It is true that none of the constants used in Equation 28 are accurately known, with the exception of the value of K' (ref. 20) in the case of the 2N $KHCO_3$ film. However, it is not reasonable to suspect that the values that were used are so much in error as to explain the wide discrepancy between experimental and predicted results. Thus, the conclusion is inescapable that the rate of one or more of the reactions involved is slow compared to the rate of diffusion. A detailed qualitative and mathematical analysis of the diffusion and reactions occurring in the film is presented in the next section. Two reactions which CO_2 undergoes in aqueous solution and which are measurably slow are

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \tag{30}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{31}$$
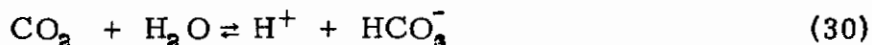
The rates, mechanisms, and catalysis of these reactions have been studied many times. The reader is referred to Kern (ref. 19) for an excellent review of the subject. The rates of reactions in Equations 30 and 31 are known very accurately and the mathematical analysis in the next section will prove that these rates (and not diffusivities) are what limit the CO_2 flux. Before the analysis was performed, however, it was proved experimentally by observing the profound effect of catalyzing the reaction in Equation 30 on the permeability of CO_2.

In a pioneering investigation, Roughton and Booth (ref. 21) found that the hydrolysis of CO_2 Equation 30 was base catalyzed. A large number of oxy-anions (but not HCO_3^- or $CO_3^=$) were found to catalyze this reaction -- sulfite, selenite, and tellurate being the most active. None of the materials tested catalyzed the reaction in Equation 31. Recently, Sharma and Danckwerts (ref. 22) made an extensive study of the catalysis of reaction in Equation 30 and concluded that arsenite is the optimum catalyst for use in industrial CO_2 absorption processes. Arsenite has a high catalytic activity, a favorable ionization constant, high solubility, and chemical stability.

The effect of $NaAsO_2$ on the permeability of CO_2 in porous cellulose acetate films impregnated with $CsHCO_3$ solution was determined. A series of measurements was made on films cut from the same large sheet that was used for the measurements on saturated $CsHCO_3$ solutions reported above. In this case, the films were impregnated with a solution that was very nearly saturated in $CsHCO_3$ and contained 0.5N $NaAsO_2$. This is approximately the solubility of $NaAsO_2$ in the $CsHCO_3$ solution used. Measurements were made on four different films. The experimental conditions were the same as those for the saturated $CsHCO_3$ films except that the partial pressure of CO_2 on the low-pressure side was varied from 0.4 to 1.3 cm Hg. Within this range there was no appreciable variation in the permeability of CO_2 and the separation factor, and the average of all of the results obtained is

$$Pr_{CO_2} = 214 \times 10^{-9} \pm 15 \text{ percent}$$

$$Pr_{O_2} = 0.052 \times 10^{-9} \pm 15 \text{ percent}$$

$$\alpha = 4100 \pm 20 \text{ percent}$$

Clearly the effect of the catalyst was to increase the CO_2 permeability. Note that the O_2 permeabilities in this and the previous experiment with no catalyst are the same, indicating that the experiments were performed on equivalent films.

These data and the previous comparisons of experimental results with Equation 28 clearly indicate that the CO_2 flux is reaction rate controlled and

21

not diffusion controlled. From this one can infer that if the film were thicker, the CO_2 permeability would be higher. In a thicker film the residence time of the diffusing CO_2 would be longer, the reactions would have more chance to occur, and facilitated CO_2 transport would be increased.

Several thick films were prepared and the CO_2 and O_2 permeabilities of the films were determined on the refined apparatus which permitted steady-state operation. The results that were obtained are presented in table IV. The experimental conditions were the same as those for the runs with saturated $CsHCO_3$ films except that the partial pressure of CO_2 on the low-pressure side was approximately 2 cm Hg.

Table IV

PERMEABILITIES OF CO_2 AND O_2 IN THICK FILMS

Solution with Which Porous Cellulose Acetate Film Was Impregnated Prior to Permeation Measurements	Film Thickness (mils)	$Pr_{CO_2} \times 100$	$Pr_{O_2} \times 10^9$	α
Saturated $CsHCO_3$	7.9	180	0.075	2400
Saturated $CsHCO_3$, 0.5N $NaAsO_2$	7.6	575	0.11	5000
Saturated $CsHCO_3$, 0.5N $NaAsO_2$	7.1	700	0.10	7000

As expected, CO_2 permeabilities were generally higher in thicker films. However, quantitative comparison between these results and previous results on 2.6- to 2.8-mil films is not possible since the film structures are not comparable. This is clear from the fact that the O_2 permeability results for the thick films were as much as two times higher than the values for the thin films.

Analysis of CO_2 Transport Across a $HCO_3^-/CO_3^=$ Film

The following discussion is concerned with the transport of CO_2 across an aqueous film containing HCO_3^- and $CO_3^=$. The three principal reactions occurring in the film are

$$CO_2 + H_2O \underset{k_1''}{\overset{k_1'}{\rightleftharpoons}} H^+ + HCO_3^- \tag{32}$$

$$CO_2 + OH^- \underset{k_2''}{\overset{k_2'}{\rightleftharpoons}} HCO_3^- \tag{33}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \tag{34}$$

22

On the side of the film exposed to a high partial pressure of CO_2 (side 1) reactions in Equations 32 and 33 tend to go to the right, and the reaction of Equation 34 tends to go to the left. Thus, CO_2 is consumed near this surface of the film and the flux of CO_2 into the film is more rapid than it would be in the absence of any reaction. At the side of the film exposed to a low partial pressure of CO_2 (side 2), the reaction in Equations 32 and 33 tend to go to the left, and in Equation 34 tends to go to the right. Thus, CO_2 is produced near side 2, and the flux of CO_2 out of the film is higher than it would be in the absence of any reaction. HCO_3^- is clearly being produced at side 1 and consumed at side 2, while $CO_3^=$ is being produced at side 2 and consumed at side 1. Thus, there is a counter diffusion of HCO_3^- and $CO_3^=$ and since the flux of HCO_3^- is twice the absolute value of the flux of $CO_3^=$, CO_2 transport across the film is augmented or facilitated by the diffusion of HCO_3^- within the film.

As pointed out previously, a considerable simplification would result if all of the reactions occurring in the film were sufficiently fast that the reacting species were present at equilibrium concentrations. In this case, surface concentrations of HCO_3^- and $CO_3^=$ would be known and from this the total CO_2 flux could be calculated. However, the reactions were not fast and the following analysis, in which an expression for the total CO_2 flux is derived, takes this into account. A differential mass balance on CO_2 at any point in the film gives

$$D_{CO_2} \frac{\partial^2 C_{CO_2}}{\partial x^2} = k_1' C_{CO_2} - k_1''(C_H^+)(C_{HCO_3^-}) + k_2'(C_{CO_2})(C_{OH^-}) \tag{35}$$

$$- k_2'' C_{HCO_3^-}$$

where the k's are reaction rate constants as shown in Equations 32 and 33. Similar mass balances can be written for the other reacting species. A solution of the resulting set of equations is not yet available.

Equation 35 could be solved easily if all of the concentrations except that of CO_2 were constant throughout the film. This would appear to be a rather drastic assumption, but it turns out to be justified. Recall that the CO_2 permeability of an aqueous film of saturated $CsHCO_3$ was 75×10^{-9}. If all of the CO_2 transport across the film is in the form of HCO_3^- and if $D_{HCO_3^-}$ is on the order of 10^{-6} cm^2/sec, then the concentration difference in HCO_3^- across the film is on the order of 10^{-2} mols/liter. Since this concentration difference is negligibly small compared to the absolute value of the average concentration of HCO_3^- in the film (evaluated below), the change in the concentrations of OH^- and H^+ across the film is negligible. Thus, it is valid to assume , for the purpose of solving Equation 34, that the concentration of HCO_3^-, H^+, and OH^- are constant throughout the film. Making this assumption, the solution of Equation 34 is

$$C_{CO_2} = \frac{A}{K_1} \sinh \sqrt{K}\, x + \frac{B}{K_1} \cosh \sqrt{K}\, x + \frac{K_2}{K_1} \qquad (36)$$

where

$$K_1 = k_2' \, C_{OH^-} + k_1'$$

$$K_2 = k_2'' \, C_{HCO_3^-} + k_1'' \, (C_{H^+})(C_{HCO_3^-})$$

$$K = K_1 / D_{CO_2}$$

$$B = K_1 \, C_{CO_2}^o - K_2$$

$$A = \frac{K_1 \, C_{CO_2}^L - K_2 - B \cosh \sqrt{K} L}{\sinh \sqrt{K} L} \qquad (37)$$

Assuming Fick's first law is valid in this system, the flux of dissolved CO_2 (not the total flux of CO_2) at any point in the film is

$$N_{CO_2} = -D_{CO_2} \frac{dC_{CO_2}}{dx} = \frac{D_{CO_2} \sqrt{K}}{K_1} (A \cosh \sqrt{K}\, x + B \sinh \sqrt{K}\, x \qquad (38)$$

The total flux of CO_2 $(N_{CO_2}^T)$ is the sum of the fluxes of dissolved CO_2, HCO_3^-, and $CO_3^=$. Since the latter two are zero at the boundaries, the equation for the total flux of CO_2 is given by Equation 38 evaluated at $x = 0$ or $x = L$. That is,

$$N_{CO_2}^T = N_{CO_2} \quad x = 0 \text{ or } x = L \qquad (39)$$

To use Equation 38 the values of the concentration of HCO_3^-, H^+, and OH^-, which are assumed to be constant, must be determined. This can be done in the following way. At steady state, the total flux of CO_2 at each boundary is the same. Evaluating Equation 38 at $x = 0$ and $x = L$ and equating the results, obtained is

$$A = \frac{B \sinh \sqrt{K} L}{1 - \cosh \sqrt{K} L} \qquad (40)$$

The condition of electrical neutrality, neglecting the small concentrations of H^+ and OH^-, requires that the following equation hold at all points in the film

$$C_{HCO_3^-} + 2C_{CO_3^=} = C_T \qquad (41)$$

Two other relations which must apply are

$$K_w = (C_{H^+})(C_{OH^-}) \qquad (42)$$

24

and

$$\frac{C_{HCO_3^-}}{(C_{H^+})\,(C_{CO_3^=})} = 1.74 \times 10^{10} \tag{43}$$

Equations 40 to 43 are four equations in four unknowns and thus, in principle, the constants necessary to predict the total CO_2 flux can be determined. However, Equation 40 is cumbersome and a simpler relationship would be desirable. For this purpose, assume that the following equation is true.

$$\frac{\partial^2 C_{CO_2}}{\partial x^2}\bigg|_{x=0} = - \frac{\partial^2 C_{CO_2}}{\partial x^2}\bigg|_{x=L} \tag{44}$$

If Equation 44 is true than A and B are related according to the following relationship:

$$A = \frac{-B(1 + \cosh\sqrt{K}\,L}{\sinh\sqrt{K}\,L} \tag{45}$$

The true relationship between A and B is given by Equation 40, but under present experimental conditions (given below) the value of $\sqrt{K}\,L$ is such that the difference between the terms

$$\frac{\sinh\sqrt{K}\,L}{1 - \cosh\sqrt{K}L} \quad \text{amd} \quad - \frac{1 + \cosh\sqrt{K}\,L}{\sinh\sqrt{K}\,L}$$

is negligible. Thus, Equation 44 is valid and from Equation 35 obtained is

$$k_1^! \, C_{CO_2}^o - k_1^{''} C_H + C_{NCO_3^-} + k^{'2} C_{CO_2}^o \, C_{OH^-} - k_2^{''} C_{HCO_3^-} \tag{46}$$

$$= - (k_1^{'} \, C_{CO_2}^L - k_1^{''} \, C_H + C_{HCO_3^-} + k_2^! \, C_{CO_2}^L \, C_{OH^-} - k_2^{''} C_{HCO_3^-})$$

Still another simplification is possible since under the present experimental conditions the terms in Equation 46 involving k_1 are negligible, thus,

$$k_2^! \, (C_{CO_2}^o + C_{CO_2} + C_{CO_2}^L)\, C_{OH^-} = 2(C_{HCO_3^-})\,(k_2^{''}) \tag{47}$$

Equations 40, 41, 42, and 47 are a set of four equations in four unknowns, the values of which can be readily evaluated and inserted into Equation 38 to predict the total CO_2 flux.

In order to compare predicted and experimental CO_2 fluxes and permeabilities, the following constants will be used, and this set of values will be defined as the standard conditions.

$$D = 2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$k_1^! = 0.026 \text{ sec}^{-1}$$

$$k_1^{''} = 5.82 \times 10^4 \text{ 1/mol, sec}$$

25

$$k_2^! \quad = \quad 2.4 \times 10^4 \; 1/mol, sec$$

$$k_2^{''} \quad = \quad 5.44 \times 10^{-4} \; sec^{-1}$$

$$C_T \quad = \quad 6.44 \; mols/1$$

$$L \quad = \quad 7 \times 10^{-3} cm$$

$$K_w \quad = \quad 1 \times 10^{-14}$$

$$\frac{(C_{H^+})\,(C_{HCO_3^-})}{C_{CO_3^=}} \quad = \quad 1.74 \times 10^{10}$$

$$C_{CO_2}^{\circ} \quad = \quad 1.34 \times 10^{-3} \; mols/1$$

$$C_{CO_2}^{L} \quad = \quad 4 \times 10^{-4} \; mols/1$$

$$\text{Solubility of } CO_2 \quad = \quad 0.03 \; mol \; 1 \; at \; 1 \; atm \; CO_2$$

The value of $k_1^!$ is from Pinsent et al. (ref. 23) and the value of $k_1^{''}$ was cal-
culated from the equilibrium constant of the reaction in Equation 32 (ref. 18).
The value of $k_2^!$ was estimated from the data of Pinsent et al. who studies
the variation of k' with the ionic strength of various salt solutions. Unfor-
tunately, cesium salts were not included in their investigation. The value
of $k_2^{''}$ was calculated from the equilibrium constant of the reaction in Equation
33 (ref. 18). The value of the solubility of CO_2 was taken to be approximately
equal to the value for pure water. The solubility of a gas in a liquid contain-
ing electrolytes with which the gas reacts is a problem that is frequently en-
countered and not easily solved. The solubility of CO_2 in several $HCO_3^-/CO_3^=$
buffer solutions was estimated by Nysing and Kramers (ref. 24) but only the
sodium and potassium salts were investigated. The cesium salts cannot be
expected to behave quantitatively the same as the sodium and potassium salts.
Thus, although the value of the solubility of CO_2 selected is undoubtedly an
upper limit of the true value, to choose any lower value would be completely
arbitrary.

The assumption has been made that the diffusivities of HCO_3^-, $CO_3^=$, and
CO_2 are the same. In view of the uncertainty in the absolute value of any of
these diffusivities, the assumption is reasonable. The particular value of
2×10^{-6} cm²/sec for the diffusivity was selected because when it is used in
the calculation of the permeability of CO_2, the calculated and experimental
results are in close agreement. The diffusivity of CO_2 in water at 25° is
1.97×10^{-5} cm²/sec (ref. 25) and the permeability of CO_2 in water at 25°
is 213×10^{-9}. The permeability of CO_2 in the porous cellulose acetate film
(discussed in Section 3 above) impregnated with pure water is 40×10^{-9}. The
solubility of CO_2 in this film is not known so that diffusivity cannot be deter-
mined accurately. However, from the value of the permeability it can be
concluded that the diffusivity of CO_2 in the film is very roughly five times
less than the value in water. The diffusivity of CO_2 in a cellulose acetate

film impregnated with a concentrated salt solution would be significantly less than in a film impregnated with pure water. Thus, the value of 2×10^{-6} cm^2/sec is not unreasonable, and is probably correct within a factor of 2.

Inserting this set of values defined as the standard conditions into Equations 40, 41, 42, and 47 and solving, the following concentrations are obtained which are the average concentrations of these species in the film.

$$[HCO_3^-] = 3.26 \text{ mols/liter}$$

$$[CO_3^=] = 1.59 \text{ mols/liter}$$

$$[H^+] = 1.18 \times 10^{-10} \text{ mols/liter}$$

$$[OH^-] = 8.50 \times 10^{-5} \text{ mols/liter}$$

Evaluating Equation 38 at $x = 0$ or $x = L$, using these values and the standard conditions one obtains the total CO_2 flux:

$$N_{CO_2}^T = 9.57 \times 10^{-10} \text{ mols/sec-cm}^2$$

from which

$$Pr_{CO_2} = 70 \times 10^{-9}$$

This value of the permeability of CO_2 is in close agreement with the value of 75×10^{-9} obtained experimentally. Agreement this close was built into the calculation by appropriate selection of the value of D, but reasonable agreement is also obtained by inserting the probable upper and lower limits of the true value of D into Equation 38. Thus, for the standard conditions and $D = 1 \times 10^{-6}$ cm^2/sec, the permeability of CO_2 is 50×10^{-9}, and for $D = 4 \times 10^{-6}$ cm^2/sec the permeability of CO_2 is 100×10^{-9}. These values represent approximate upper and lower limits of the true value of the permeability of CO_2. Since the experimental value falls within this range, it can be concluded that the analysis leading to Equation 38 is sufficiently accurate to be useful in predicting, at least semiquantitatively , the permeation characteristics of the film as a function of several key variables of the system.

The following permeation characteristics of $CsHCO_3/Cs_2CO_3$ film were obtained by the use of Equation 38. Except for the one requirement which was varied, the requirements used in Equation 38 were those which represent the standard conditions, as defined above.

(1) The effect of the rate of the reaction

$$CO_2 + H_2O \underset{k_1''}{\overset{k_1'}{\rightleftharpoons}} H^+ + HCO_3^-$$
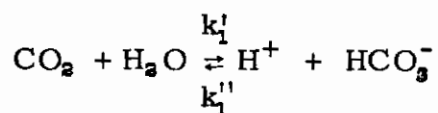
on the permeability of CO_2 and the separation factor is shown in figure 5. The value k_1' was varied from 0.026 to 10 sec^{-1}, and the value of k_1'' was

varied such that the equilibrium constant of the reaction was not changed. It was assumed that the permeability of O_2 is constant at 0.05×10^{-9}. Note that for increasing values of $k_1^!$, the permeability of CO_2 and separation factor rise slowly at first, and then at larger values of $k_1^!$ they increase very rapidly. This is to be expected since with no catalyst present ($k_1^! = 0.026$) the velocity of the hydrolysis of CO_2 is negligible compared to the velocity of the reaction $CO_2 + OH^- \rightleftarrows HCO_3^-$.

The value of $k_1^!$ (and $k_1^{!!}$) was varied experimentally by the addition of catalysts, the best of which was an arsenite. Unfortunately it is not possible to compare the experimental and predicted results since the only quantitative estimates of the catalytic activity of arsenite are grossly different (ref 22 and 26) and none of the work was carried out at 25 C.

(2) The effect of film thickness on the CO_2 flux and the separation factor is shown in figures 6 and 7. Note that the CO_2 flux is essentially constant for $L > 0.005$. This is another indication that the CO_2 flux is reaction rate controlled. For $L > 0.015$ the assumption of a constant concentration of HCO_3^- in the film is no longer valid.

Earlier in this section, the experimentally determined permeation characteristics of several thick films were presented. As this analysis predicts they should be, the CO_2 permeabilities were generally higher in thicker films. However, quantitative comparison between the set of results for thick films and the set for thin films is not feasible because the film-structures were not comparable.
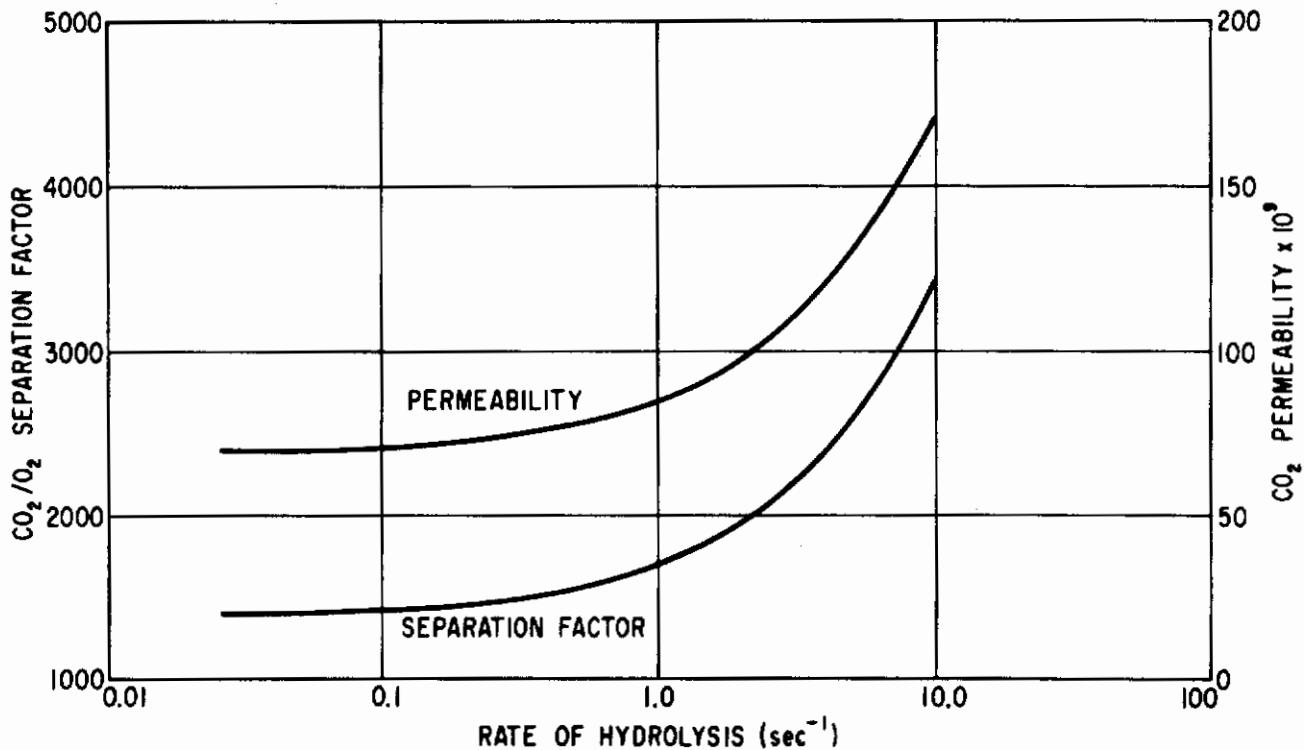

Figure 5.   Effect of the rate of hydrolysis of CO_2 on the CO_2 permeability and the CO_2/O_2 separation factor.
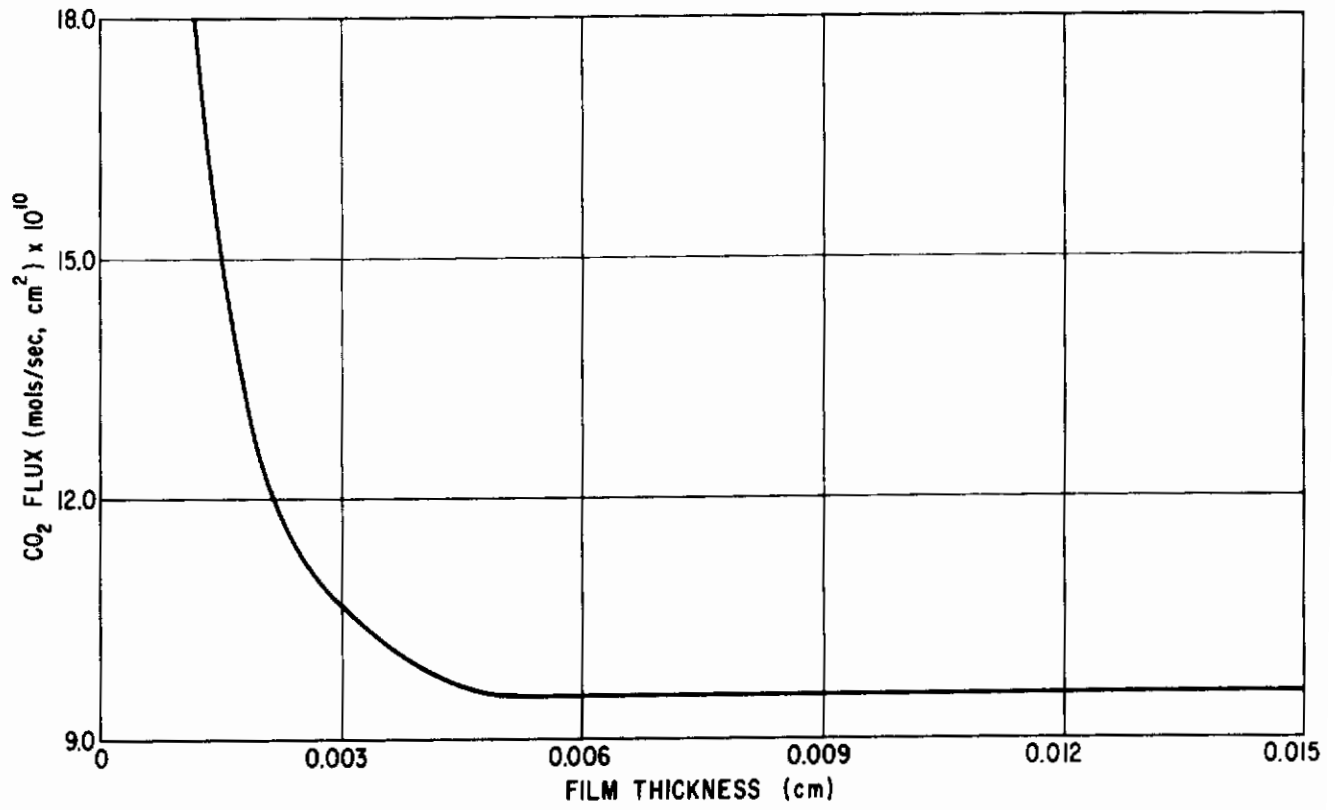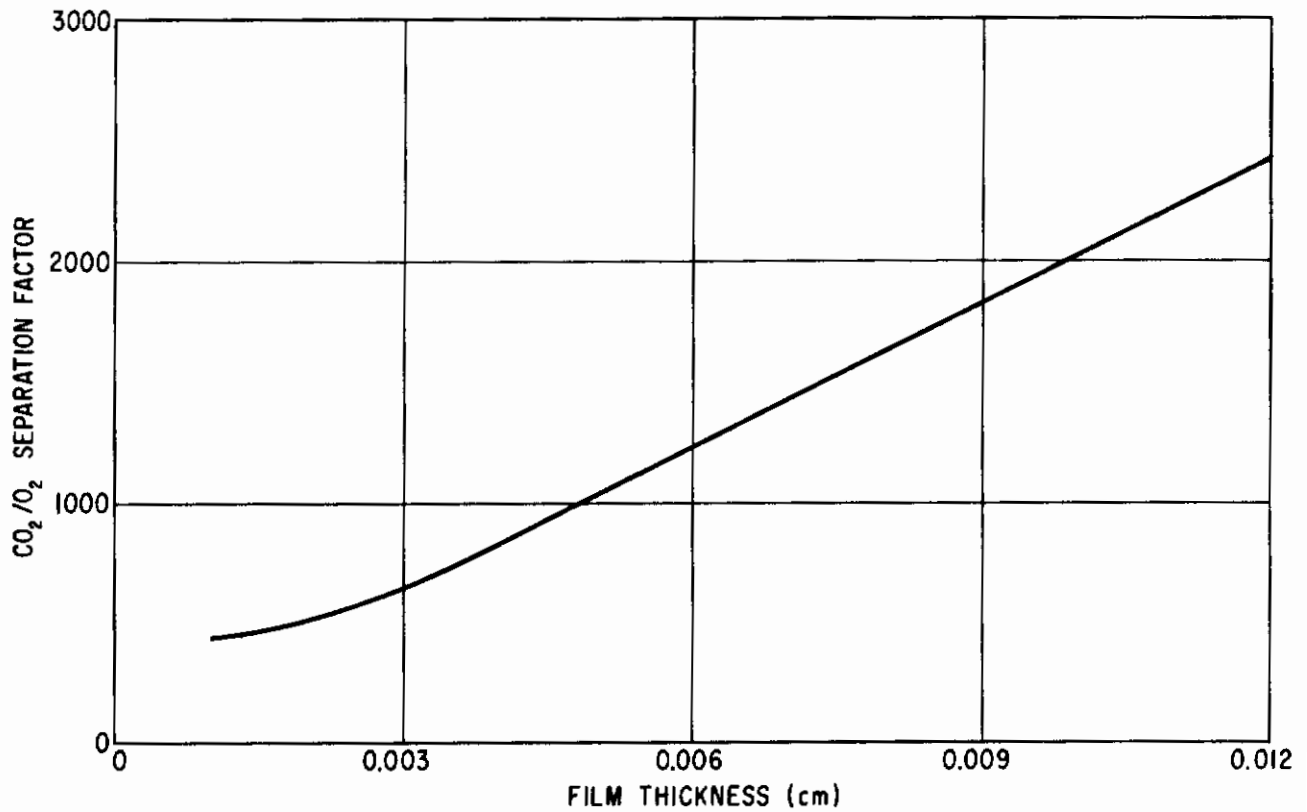
Figure 6. Plot of CO_2 flux vs film thickness.

Figure 7. Plot of CO_2/O_2 separation factor vs film thickness.

29

(3) The variation of the permeability of CO_2 with the partial pressure of CO_2 on the low-pressure side of the film

$$PP_{CO_2}^L$$

at two values (3.4 and 0.7 cm Hg) of the partial pressure of CO_2 on the high-pressure side of the film

$$PP_{CO_2}^o$$

is shown in figure 8. The value of 3.4 cm Hg for

$$PP_{CO_2}^o$$

is the same as the experimental value used throughout this investigation. The value of 0.7 cm Hg for

$$PP_{CO_2}^o$$

is approximately the value which would be encountered in a manned space-craft.

In figure 9 the separation factor is plotted as a function of the same parameters as in figure 8. The permeability and selectivity of the membrane for CO_2 generally improve with decreasing values of
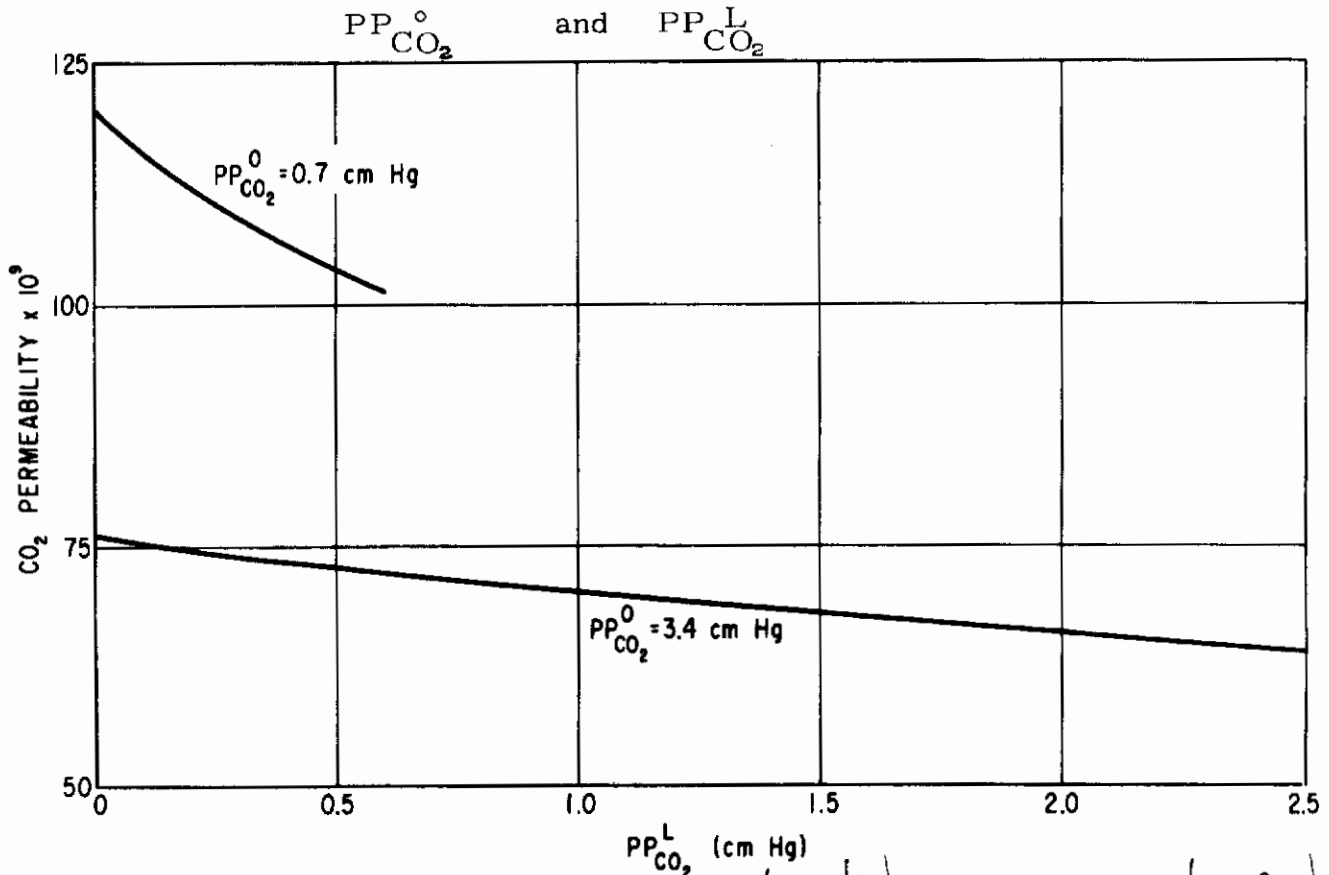
$$PP_{CO_2}^o \quad \text{and} \quad PP_{CO_2}^L$$

Figure 8. Plot of CO_2 permeability versus $\left(PP_{CO_2}^L\right)$ at two values of $\left(PP_{CO_2}^o\right)$.
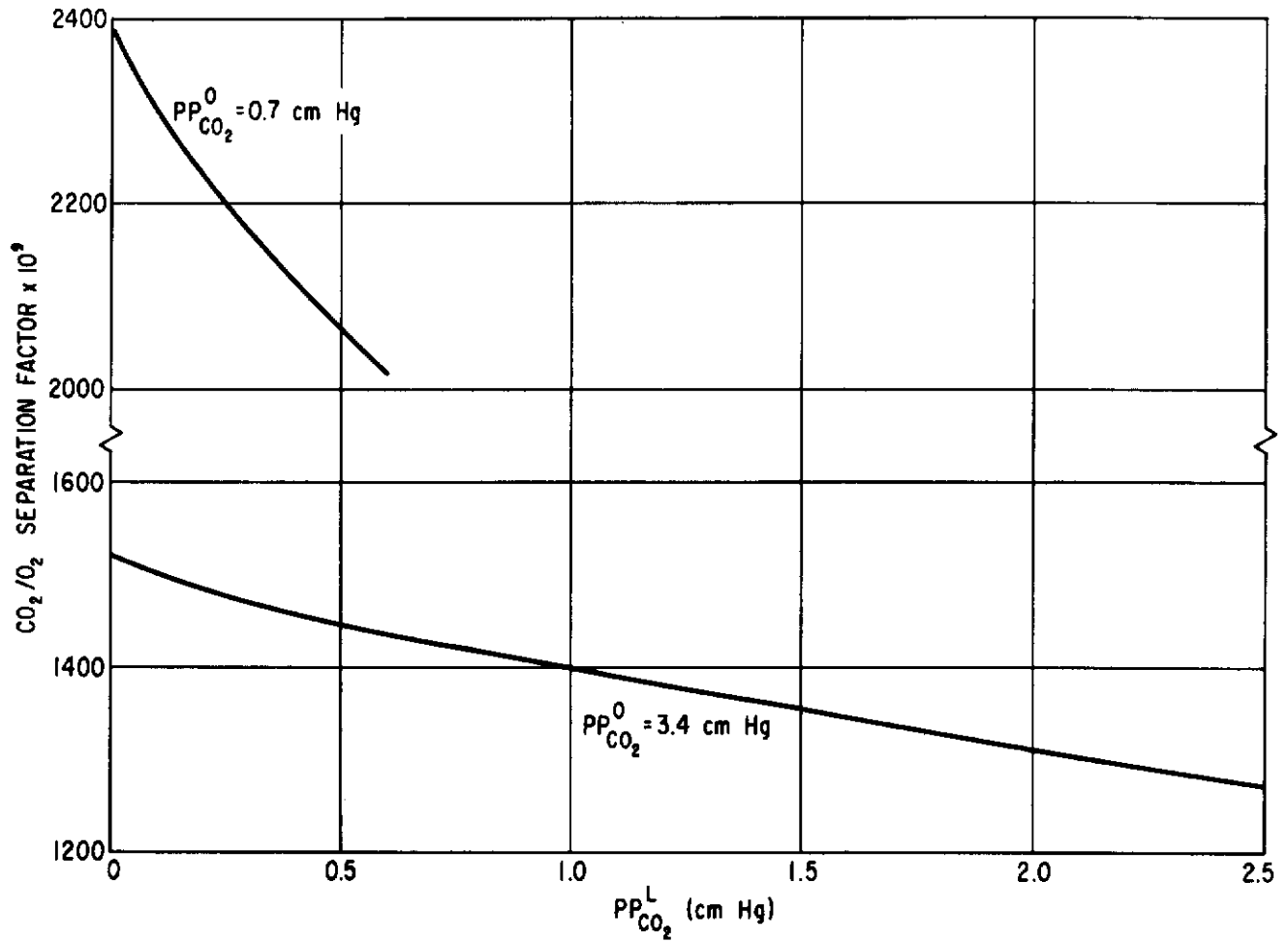
Figure 9. Plot of CO_2/O_2 separation factor vs $\left(PP^L_{CO_2}\right)$ at two values of $\left(PP^0_{CO_2}\right)$.

CONCLUDING REMARKS

The best polymeric membrane for CO_2/O_2 separation is silicone rubber which combines a CO_2/O_2 separation factor of 5.5 and a CO_2 permeability of 300×10^{-9}. This is not a sufficiently high separation factor to make practical a membrane system for CO_2 removal from a manned spacecraft.

Liquids, which in this investigation have been considered as potential membrane materials, in some cases have permeation characteristics not found in any polymeric materials. For example, pure water has a CO_2 permeability of 210×10^{-9} and a CO_2/O_2 separation factor of 22. No pure liquid has substantially better permeation characteristics for CO_2/O_2 separation than pure water.

An immobilized film of water is available in the form of a modified cellulose diacetate film, first fabricated by Loeb and Sourirajan in 1960 for use in a reverse osmosis process for desalination. A similar film, fabricated in this laboratory, containing 60 percent water had a separation factor of 20 and a CO_2 permeability of 40×10^{-9}. The film was tough, contained no pinholes, and could be made as thin as 1 mil.

The flux of CO_2 across an aqueous film can be augmented by the diffusion of HCO_3^- across the film in the same direction as the CO_2 transport. In the most effective means of accomplishing this, an alkali bicarbonate was added to the film. An additional effect of the salt was to decrease the permeability of O_2. The CO_2 flux was reaction rate limited and the addition of a catalyst of the reversible hydrolysis of CO_2 to the film substantially increased the CO_2 permeability. Thus, under the experimental conditions of the present investigation, a 2.6 mil film of porous cellulose acetate impregnated with a 6.4-N $CsHCO_3$ plus 0.5-N $NaAsO_2$ solution had a separation factor of 4100 and a CO_2 permeability of 214×10^{-9}.

The development of this membrane will make it possible to build a simple, compact, lightweight membrane device with a low power requirement which will concentrate the CO_2 present in the atmosphere of a spacecraft at approximately 1 percent to over 95 percent in one pass through the membrane.

It may be possible to develop practical membrane systems for important gas separations in addition to CO_2/O_2 by extending the principle of facilitated transport, which this work has demonstrated.

32

PERMEABILITY MEASUREMENTS IN PURE LIQUIDS

A sketch of the apparatus used to measure permeabilities in pure liquids is shown in figure 10. The liquid film was supported on a 1-mil silicone rubber membrane which in turn was supported by a porous stainless steel disc. To measure a permeability, a known volume of liquid was placed on the silicone rubber membrane. Region (A) was evacuated to a pressure of 10μ or less, and the valve to the vacuum pump was closed. Region (A) was then saturated with liquid from bulb (B) and the valve to the bulb was closed. Gas at 1 atm, which was presaturated with the same liquid as that used for the film, was gently circulated over the liquid film. The buildup of pressure in (A) was recorded by measuring with a cathetometer the mercury level in the manometer. The change in volume of region (A) during the run was negligible. The resistance of the silicone rubber film to the permeation of the gas was negligible compared to the resistance of the liquid film. Knowing the liquid film thickness, the area for permeation, the volume of region (A), and the rate of pressure buildup, the permeability of gas in the liquid was calculated.
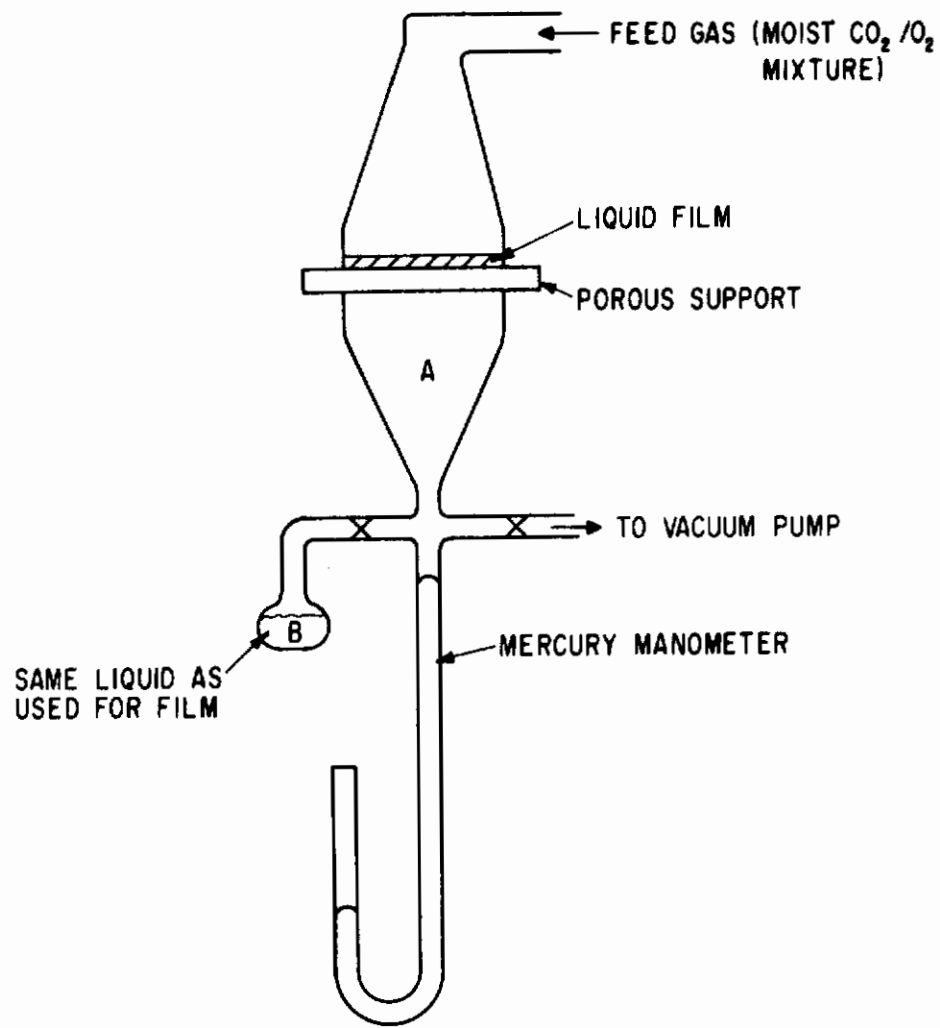
Figure 10. System for measuring permeabilities of liquid films.

PROCEDURE FOR STEADY-STATE DETERMINATION
OF CO_2 AND O_2 PERMEABILITIES

A diagram of the equipment used for steady-state permeation measurements is shown in figure 11. A dry mixture of CO_2 and O_2 was bubbled through a sulfuric acid solution (not shown in figure 11) and then fed to the permeation cell. The strength of the acid solution was such that the partial pressure of water in the feed was in equilibrium with the partial pressure of water in the film. As discussed in Section 3 it was desirable to back the cellulose acetate film with a 1-mil silicone rubber film to minimize water transport through the cellulose acetate. Gas permeating through the film passed into region A and then through a controlled leak valve. The total pressure in A was measured by sighting on a U-tube mercury manometer with a cathotometer. The pressure in A was in the range of 2 to 4 cm Hg. The system was at steady state when the pressure in A and the opening of the controlled leak valve were such that the rate at which gas entered A through the film equalled the rate at which it left A through the controlled leak valve.

The downstream side of the controlled leak valve was maintained at essentially a vacuum. Sampling of the gas passing through the film was accomplished by closing valve (b) to the vacuum pump, closing valve (c), and opening valves (a) and (d). The pressure was allowed to build up in the sample bulb to several hundred microns of Hg which was not enough to affect conditions upstream of the constant leak valve. After the pressure buildup in the sample bulb, valves (a) and (d) were closed and valve (b) to the vacuum pump was reopened. The bulb was removed from the system and its contents were analyzed on a mass spectrometer to determine the ratio of the partial pressures of CO_2 and O_2.

A rate determination was performed by closing valves (b) and (a) and opening valve (c). This caused a pressure buildup in region B which was monitored by the resulting movement of the oil level in the inclined arm of the manometer. Region C of the inclined manometer was always at a vacuum. The ratio of diameters of the large- and small-diameter tubes of the manometer, the inside diameter of the small-diameter tube, and the density of the oil were such that when the pressure in region B increased 26μ of Hg the oil level moved 1 cm. A scale was positioned behind and parallel to the incline tube to read the position of the oil level in the tube. Pressure was allowed to build up in region B for a measured time interval, and the change in position of the oil level in the incline tube was noted. This pressure buildup had no effect on conditions upstream of the controlled leak valve. Valve (c) was closed and valve (b) was reopened. At this point the sum of the rates at which CO_2, O_2, and water vapor were permeating through the film was known. The water vapor in region B was removed by surrounding the cold finger in a dry ice-acetone bath. This caused the oil level in the incline tube of the manometer to move to the left and the final position of the
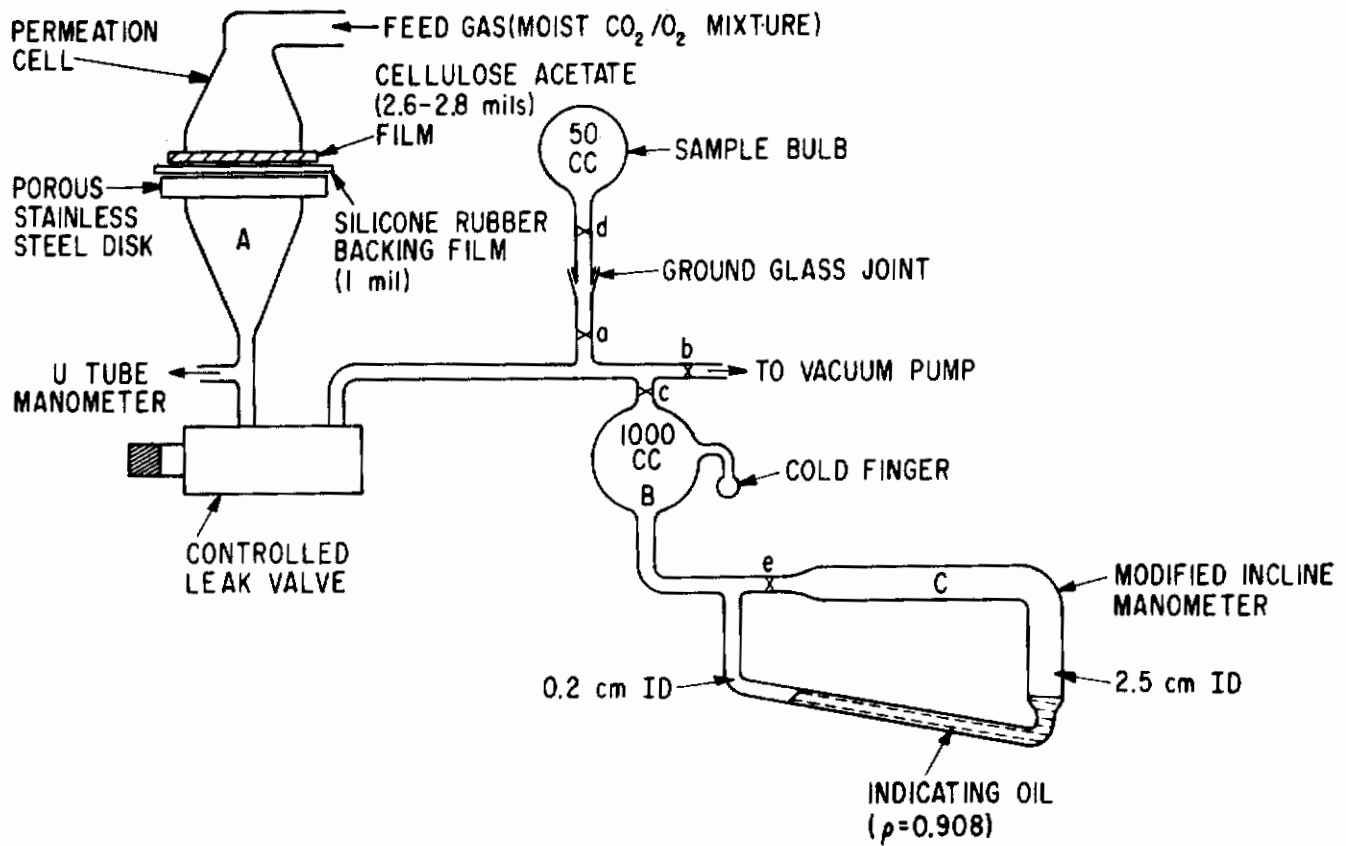
Figure 11.   Equipment for permeation measurement
under steady-state conditions.

oil level was noted.   At this point the sum of the rates at which CO_2 and O_2 were permeating the film could be calculated.   From this information plus the mass spectrometer analysis of the product gas, the partial pressure of CO_2 and O_2 in region A could be calculated, and from this the permeability of CO_2 and O_2 and the CO_2/O_2 separation factor could be calculated.

1. Kohl, A. L., and Riesenfeld, F. C., "Today's Processes for Gas Purification," Chemical Engineering, Vol. 66, No. 12, 1959, p.127.

2. Quinn, E. L., and Jones, C. L., Carbon Dioxide, Reinhold Publishing Company, New York, 1936.

3. Solubilities of Inorganic and Organic Compounds, Macmillan Company, New York, 1963.

4. Loeb, S. S., and Sourirajan, S., "Sea Water Demineralization by Means of an Osmotic Membrane", Advanced in Chemistry Series, Vol. 38, 1962, p. 117.

5. Olander, D. R., "Simultaneous Mass Transfer and Equilibrium Chemical Reaction," AIChE Journal, Vol. 6, 1960, p. 233.

6. Osterhout, W. J. V., "Studies of Some Fundamental Problems by the Use of Aquatic Organisms," Annual Review of Physiology, Vol. 20, 1958, p.1.

7. Scholander, P. F., "Oxygen Transport through Hemoglobin Solutions," Science, Vol. 131, 1960, p. 585.

8. Wittenberg, J. B., "Oxygen Transport - A New Function Proposed for Myoglobin," Biological Bulletin, Vol. 117, 1959, p. 402.

9. Fatt, I., and LaForce, R. C., "Theory of Oxygen Transport through Hemoglobin Solution," Science, Vol. 133, 1961, p.1919.

10. Zilversmit, D. B., "Tension Gradients Accompanying Accelerated Oxygen Transport in a Membrane," Science, Vol. 149, 1965, p.876.

11. Wittenberg, J. B., "The Molecular Mechanism of Facilitated Oxygen Diffusion," Journal of Biological Chemistry, Vol. 241, 1966, p. 104.

12. Wyman, J., "Facilitated Diffusion and the Possible Role of Myoglobin as a Transport Mechanism," ibid., p. 115.

13. Keller, K. H., and Friedlander, S. K., "The Steady-state Transport of Oxygen through Hemoglobin Solutions," Journal of General Physiology, Vol. 49, 1966, p. 663.

14. LaForce, F. C., "Steady-State Diffusion in the Carbon Monoxide + Oxygen + Hemoglobin System," Transactions of the Faraday Society, Vol. 62, 1966, p. 1458.

15. Wittenberg, J. B., "Myoglobin-facilitated Diffusion of Oxygen," Journal of General Physiology, Vol. 49, 1965, p. 57.

16. Adair, G. S., Bock, A. V., and Field, H. Jr., "The Hemoglobin System. Part 6: Oxygen Dissociation Curve of Hemoglobin," Journal of Biological Chemistry, Vol. 63, 1925, p. 529.

17. Sherwood, T. K., and Pigford, R. L., Absorption and Extraction, McGraw-Hill Book Company, Inc., New York, 1952.

18. Stability Constants, Special Publication No. 17, Chemical Society, London, 1964.

19. Kern, D. M. H., "The Hydration of Carbon Dioxide," Journal of Chemical Education, Vol. 37, 1960, p. 14.

20. Walker, A. C., Bray, V. B., and Johnston, J.,"Equilibrium in Solution of Alkali Carbonates," Journal of the American Chemical Society, Vol. 49, 1927, p. 1235.

21. Roughton, F. J. W., and Booth, V. H., "The Catalytic Effect of Buffers on the Reaction $CO_2 + H_2O = H_2CO_2$," Biochemical Journal, Vol. 32, 1938, p. 2049.

22. Sharma, M. M., and Danckwerts, P. V., "Catalysis by Brönsted Bases of the Reaction Between CO_2 and Water," Transactions of The Faraday Society, Vol. 59, 1963, p. 386.

23. Pinsent, B. R. W., Pearson, L., Roughton, F. J. W., "The Kinetics of Combination of Carbon Dioxide With Hydroxide Ions," ibid, Vol. 52, 1956, p. 1512.

24. Nysing, R. A. T. O., and Kramers, H., "Absorption of CO_2 in Carbonate-bicarbonate Buffer Solutions in a Wetted Wall Column," Chemical Engineering Science, Vol. 8, 1958, p. 81.

25. Scriven, L. E., and Pigford, R. L., "On Phase Equilibrium at the Gas-liquid Interface During Absorption," AIChE Journal, Vol 4, 1958, P439

26. Sumner, J. B., and Myrback, K., eds., The Enzymes, Vol. 1, Part 2, Academic Press, New York, 1951, p. 1251.

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Research and Development Center General Electric Company Schenectady, N. Y.	UNCLASSIFIED
	2b. GROUP N/A

3. REPORT TITLE

IMMOBILIZED LIQUID MEMBRANES FOR CONTINUOUS CARBON DIOXIDE REMOVAL

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report - July 1965 to June 1966

5. AUTHOR(S) *(Last name, first name, initial)*

Ward, W. J., III

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
		26

8a. CONTRACT OR GRANT NO. AF-33(615)-2957	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 6373	S-67-1076
c. Task No. 637302	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	AMRL-TR-67-53

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited. It may be released to the Clearinghouse, Department of Commerce, for sale to the general public.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Aerospace Medical Research Laboratories Aerospace Medical Div., Air Force Systems Command, Wright-Patterson AFB, O. 45433

13. ABSTRACT

The objective of this program was the development of an immobilized liquid membrane for CO_2 removal from a manned spacecraft. During basic film research, water was found to be better than a polymeric material or any pure liquid for CO_2/O_2 separation. An immobilized film of water was available in the form of a porous cellulose acetate membrane fabricated at the Research and Development Center. By impregnating this membrane with a concentrated solution of $CsHCO_3/Cs_2CO_3$, and a catalyst for the hydrolysis of CO_2, CO_2 transport was facilitated and O_2 transport was decreased to obtain a CO_2/O_2 separation factor and CO_2 permeability of 4100 and $214^2 \times 10^{-9}$. A mathematical analysis of CO_2 transport was also carried out. It will now be possilbe to build a single-stage CO_2 removal system with minimum power, weight, and size requirements.

DD FORM 1473 1 JAN 64

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gas separation Facilitated transport Membranes						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.