The Permeation of Carbon Dioxide, Oxygen, and Nitrogen Through Weakly Basic Polymer Membranes

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Permeation, diffusion, and solubility coefficients were measured for carbon dioxide, O_2 and N_2 in the four component membrane system, polyethylenimine—polyvinylbutyral—epoxy (Epon 834)—water, using a variable pressure technique. Extremely high CO_2/O_2 and CO_2/N_2 selectivity ratios were obtained. This can be attributed to reversible reactions between the carbon dioxide, water, and polyethylenimine which markedly increases the carbon dioxide solubility in the membrane with respect to those of O_2 and N_2. The O_2 and N_2 permeation occurs in the classical manner.

The high carbon dioxide selectivity coupled with the good O_2 permeability of this membrane makes it potentially useful in an atmospheric control system or in a blood oxygenator.

The purpose of this investigation was to determine the feasibility of using a weakly basic ion exchange membrane system to selectively remove carbon dioxide by gas permeation from mixtures containing carbon dioxide, nitrogen and oxygen in the gas phase and also in solution. With the advent of vehicles such as submarines and space craft which remove man from his natural environment for long periods of time, special methods are necessary to sustain him in a small finite atmosphere. In particular it is important that the water and carbon dioxide continuously introduced into the atmosphere can be continuously and efficiently removed.

For various reasons, present practices are inadequate. Monoethanolamine scrubbers in use in submarines utilize a toxic, volatile, combustible liquid and require high power loads. Lithium hydroxide scrubbers involve an irreversible reaction, thus requiring large inventories of fresh material. Another potential use for the system under investigation here is in blood oxygenation. Membrane blood oxygenators in present use are extremely inefficient in removing carbon dioxide from blood while allowing the entry of oxygen. One reason for this inefficiency lies in the poor mixing characteristics within the system but a second reason lies in the low permeability of membranes in present use to carbon dioxide.

The basis for the present work was laid by Robins (*1*) who showed that dilute aqueous solutions of polyamines exhibit a high capacity for carbon dioxide absorption. Based on this finding, Saber (*2*) synthesized a solid ion exchange resin from polyethylenimine, and Weber et al. (*3*) evaluated its potential use as a carbon dioxide absorbent for a recirculated air system. While the resin exhibited a reasonable carbon dioxide absorption capacity, the diffusion of carbon dioxide into the interior of the resin particle appeared to be the rate limiting step.

In an attempt to increase the diffusion of carbon dioxide into the resin system, Wolfe et al. (*4*) cast the resin in membrane form to take advantage of the highly open structure of such a formulation. They found that the carbon dioxide absorption capacity of the film was increased markedly over the values obtained by Weber and in fact found a diffusion coefficient for carbon dioxide of five times that measured for the ion exchange resin of Weber. In addition, Wolfe measured the permeability of the film to carbon dioxide and O_2 and found that the permeability ratio of these two gases was many times greater than that of most commercial materials. It is the investigation of this particular property that is reported herein.

EXPERIMENT

The membranes used in this study were made with polyethylenimine (PEI) of a molecular weight of approximately 1800, and polyvinylbutyral (PVB) as the film former. Cross linking was provided by the use of enough epoxy to form at least two cross links per chain. The cross linking agent was Shell Epon 834, this being the lowest molecular weight diepoxide available that would form homogeneous membranes.

The ingredients were dissolved in a compatible mixed solvent system. The membranes were cast on glass plates using a Gardner film casting knife. The cast membranes were dried in the oven and removed from the casting surface by soaking in water. The membranes were treated with 1M NaOH (to activate the imine groups) and then washed in distilled water until the *p*H became constant (at *p*H 11). The membranes were equilibrated with air of the desired humidity until ready for use.

The membrane formulation variables studied included the relative amounts of the solid ingredients in the casting solution (the PEI-PVB ratio was varied from 0 to 4), the total solids contents of the casting solution (varied from 2% by weight to 20% by weight), the drying temperature (varied from 25° to 70°C. and included some experiments with vacuum drying), and the use of LiCl additives in amounts ranging from 0.5 to 5.0% by weight of the dried membrane in an attempt to change the membrane permeability.

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The permeability coefficient, diffusion coefficient, and solubility coefficient of the gases of interest were measured in the membranes by use of a standard variable pressure diffusion cell and accompanying peripheral equipment as shown in Figures 1 and 2.

The cell, a cylinder 5 cm. in diameter and 15 cm. long, consisted of two sections separated by the membrane and its Vexar (DuPont brand of plastic screening) support. An obstruction on the high pressure side insured that the gas flow was parallel to the membrane.

The vacuum on the low pressure side was obtained by means of a high vacuum pumping station (Type VS-9, Vacuum Electronics Corporation). The unit also contained a thermocouple gauge (Type DV-1M, Vacuum Electronics Corporation), an ionization gauge (Type RG-75, Vacuum Electronics Corporation), and a manometer to monitor the pressure rise in the low pressure section after the valve separating the cell from the vacuum line is closed.

In making an experiment, the membrane was inserted between the flanges in the cell, the cell was closed and tightened by means of four bolts on the flanges. A rubber gasket was used to insure a vacuum tight seal. After the cell was leak tested, O_2, N_2, or carbon dioxide obtained from cylinders of 99.6% minimum purity supplied by the Matheson Company was passed through humidifiers to achieve the desired humidity level. This level was measured by means of wet and dry bulb thermometers and was controlled by adjusting the fraction of gas which bypassed the humidifiers. The heat input into the humidifiers was also under control. The humidified gas was then passed into the high pressure side of the cell. The cell temperature was controlled to ± 0.1°C. by means of a simple on-off controller attached to immersion heaters in the constant temperature bath surrounding the cell. The flow rate was measured by a calibrated dry test gas meter and pressure gauges were used to measure pressure.

The pressure on the low pressure side of the cell was measured as a function of time after the gas started passing through the cell. From this pressure-time curve, the permeability, diffusion, and solubility coefficients can be determined.

In order to determine the effect of gas flow rate on the high pressure side on measured membrane permeabilities, experiments were performed at several flow rates. The calculated values of diffusivities turned out to be independent of gas flow rate down to the lowest practically achievable flow rate (~ 30 cc./sec.), and so, it was assumed that the membrane provided the controlling resistance to permeation.

Since water was always present in these experiments, it was important to account for any effect of water flux on the measured gas permeabilities. In order to minimize this effect, the entire system was equilibrated with water vapor at the appropriate humidity (usually 100% RH) for several hours before each experiment. In the 100% humidity runs, which made up the bulk of this work, a small amount of liquid water was always present in the high pressure chamber, and the entire cell was allowed to come to water content equilibrium before the test gas was introduced. In all the experiments involving O_2 flux, the pressure rise was monitored both with the pressure gauges and also with a Westinghouse Oxygen Gauge, model 203A. No detectable differences between these two measurements were noted. On this basis, it was assumed that water flux made a negligible contribution to the gas pressure rise measurements.

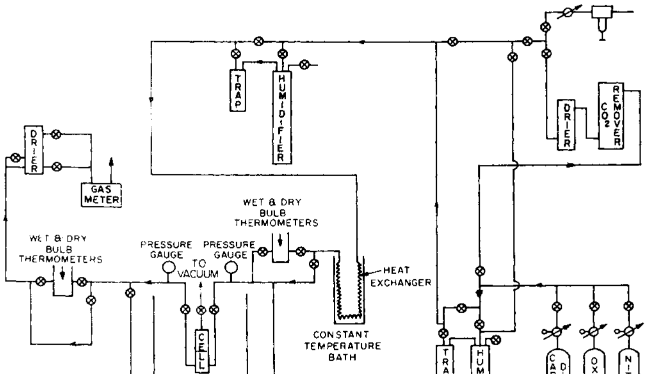

Fig. 1. Flow diagram for diffusion measurements.

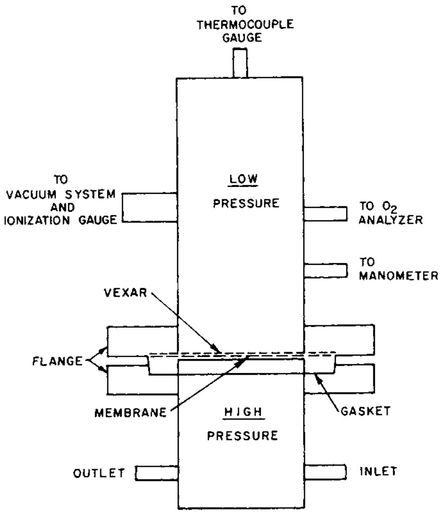

Fig. 2. Diffusion cell.

CALCULATION PROCEDURE

The permeability coefficient P is defined as the amount of gas at standard temperature and pressure passing through a membrane of unit thickness per unit time per unit area per unit driving force. It was calculated from low pressure side pressure versus time data using the equation

$$P = \frac{(\Delta P)(V_c)(L)(273)}{(\Delta t)(A)(T)(P_d)(76)} \tag{1}$$

The apparent diffusion coefficient D of the gas in the membrane was calculated using the time lag method of Daynes (5) and Barrer (6). In this method the straight portion of the pressure time curve is linearly extrapolated back to the time axis. The intercepts of the line on the time axis θ is related to D by the equation

$$D = \frac{L^2}{6\theta} \tag{2}$$

Since by definition

$$P = D\ S \tag{3}$$

the solubility coefficient S (cc.'s of gas per cc. of membrane per unit pressure) can be obtained from the following equation

$$S = \frac{P}{D} \tag{4}$$

There are a number of assumptions implicit in the use of these procedures. Chief among these is the assumption that the carbon dioxide, in bicarbonate form, is immobilized by reversible reaction with the imine sites essentially instantaneously when compared to the diffusion rate, with equilibrium present throughout. This assumption is an outgrowth of the work of Weber (3) and Wolfe (4), in which absorption of carbon dioxide by imine resins was studied. In both of these works, a multiphase model was used with the following four-step mechanism:

1. Transfer of carbon dioxide from the bulk gas to a liquid film on the membrane and instantaneous conversion to bicarbonate form, with equilibrium established.

2. Transfer of bicarbonate across the liquid film via a linear concentration gradient.

3. Slow diffusion into the matrix governed by Fick's Law.

4. Instantaneous reversible reaction of bicarbonate with the fixed imine sites, with equilibrium at all interfaces.

Using this model, both Weber and Wolfe were able to obtain excellent correlations with data. In addition, Wolfe compared the apparent diffusion coefficients for carbon dioxide, calculated by use of the model with those measured at the same temperature by the time lag method and obtained excellent agreement. While this is no proof that the assumptions are valid, it does indicate the reasonableness of the approach.

Another approach might be to model the system as a facilitated diffusion process as, for example, discussed by Ward (7). In such a process, the diffusing specie is assisted across the membrane by reaction with a carrier which diffuses independently. For example, bicarbonate might be considered a carrier for carbon dioxide. There are a number of arguments against such a model. First of all, at *p*H 11 (the ambient condition), essentially all the carbon dioxide is in bicarbonate form, so there is only one form of diffusing carbon dioxide. Secondly, the imine groups with which the bicarbonate reacts are part of the membrane matrix and so, the bicarbonate-imine complex can only serve to immobilize the diffusing specie, not facilitate its diffusion. For these reasons, a facilitated diffusion model for the process was rejected.

In an attempt to verify the view that the effects observed are a solubility effect alone and not facilitated transport, a comparison was made of a set of membrane solubilities calculated from Equation (4) with those measured directly on the same membranes. For these experiments, five membranes made of formulations ranging from 5 to 20% solids content, all with a 2/1 PEI/PVB ratio, were involved. All permeability and time lag measurements were at 30°C. and 100% RH conditions and involved carbon dioxide only. (The solubilities of O_2 and N_2 were too low to allow a precise static measurement.)

For the static measurements, samples of the membrane about 6.5 cm. in diameter and 0.15 mm. thick were placed in the diffusion cell (unmounted on the flanges) and the cell was pressurized to 10-15 cm. Hg above atmospheric with humidified carbon dioxide and sealed. The pressure was monitored until it became constant (typical pressure losses ranged from 6-15 cm. Hg) and the apparent static solubility of carbon dioxide in the membrane was calculated from the pressure loss. A comparison of the static solubility measurements with those calculated from Equation (4) is shown in Table 1.

If facilitated diffusion occurs, then the time lag method, as we have employed it, is inapplicable. Thus, the carbon dioxide solubilities calculated using Equation (4) would also be incorrect. The results shown in Table 1 indicate quite good agreement between calculated and measured values of carbon dioxide solubility (with the exception of one point) and add extra weight to the model presented above.

TABLE 1. COMPARISON OF MEMBRANE SOLUBILITIES FOR CO_2 MEASURED STATICALLY WITH THOSE CALCULATED FROM EQUATION (4)

(PEI/PVB ratio = 2, 30°C., 100% RH)

Membrane	% Solids in casting solution	S_{calc}	S_{exp}
1	5	0.672	0.67
2	5	0.659	0.75
3	10	0.643	0.53
4	20	0.696	0.94
5	20	0.729	0.79

RESULTS

Effect of Temperature

Measurements of permeability coefficients, diffusion coefficients and solubility, respectively, for carbon dioxide, O_2, and N_2 for two different membranes are shown in Figures 3, 4, and 5 as a function of the temperature at which the process took place. For the membranes shown on these figures, the casting solution consisted of a 2:1 PEI to PVB ratio by weight, and contained either 20% solids or 5% solids. The membranes were formed by drying at 50°C. without lithium chloride additive and were equilibrated to 100% relative humidity. Transport measurements on these membranes were made at temperatures varying from 25° to 45°C. An inspection of Figures 3, 4, and 5 leads to some interesting conclusions.

Values of permeability coefficient, diffusion coefficient and solubility as a function of temperature are well represented by an Arrhenius type of equation with *P* and *D* increasing with increasing temperature while *S* decreases. Such results are typical for this type of data with any membrane system. The exceptional features of this particular membrane system are the difference in the apparent activation energies for diffusion for carbon dioxide as compared with those for O_2 and N_2, and the extremely high values

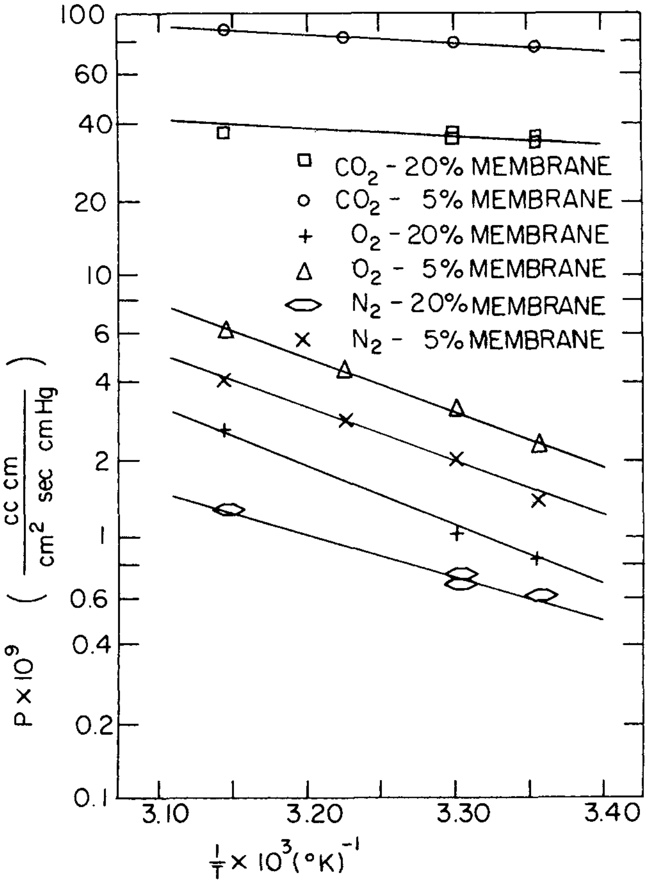

Fig. 3. Permeability coefficients versus temperature, (*PEI/PVB* = 2).

for the activation energy for diffusion for O_2 and N_2 compared to what is normally obtained in water. The extremely high permeability coefficient for CO_2 as compared to O_2 and N_2 shown in Figure 3 is readily seen to be a solubility effect entirely, as is demonstrated in Figure 5. The activation energies for diffusion obtained from Figure 4 are given in Table 2.

Typical values for the activation energy for diffusion for gases through liquids are in the range of 2 to 5 kcal./mole. Helfferich (*8*) has given typical activation energies for diffusion through ion exchange resins in the range of 6 to 10 kcal./mole. In the membranes studied here with measurements made at 100% relative humidity, diffusion takes place mainly through the water contained in the membrane pores. Evidence for this assertion comes from Table 3 which presents water content (measured by weight) of a membrane as a function of percent relative humidity for a 20% solids, 2:1 PEI/PVB ratio membrane. These membranes are highly hygroscopic and swell significantly in the presence of water vapor. The apparent high values for the activation energy for diffusion for O_2 and N_2 can be attributed to the effect of the polymer matrix on the structuring of pore water. The structuring of water near solid surfaces is discussed in detail by Drost-Hansen (*9*). If there is significant structuring of pore water in these membranes, significantly greater amounts of energy would be required for a solute molecule to migrate that would be the case without such structuring. The exclusion of salts from reverse osmosis membranes has often been attributed to just this type of structuring (*10*).

If such arguments for water structuring in the case of O_2 and N_2 are accepted, clearly the mechanism by which carbon dioxide transports across these membranes must be quite different. In the case of carbon dioxide, it is postulated that the following reversible chemical reactions take place within the membrane system

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad (5)$$

$$\left[CH_2 - CH_2 - NH_2^+ \right] + HCO_3^- \rightleftarrows \text{complex} \qquad (6)$$

Evidence for these reactions comes from several sources including Weber and Wolfe. Figure 5 indicates an enormously increased solubility of carbon dioxide in these membranes over what one would expect for either neutral membranes or for pure water. This solubility can be attributed to the immobilization of the carbon dioxide in bicarbonate form within the membrane matrix. At the ambient basic conditions (*p*H 11), essentially all of the carbon dioxide will be in bicarbonate form, either mobile in the pore water or bound within the membrane matrix. Figure 6, showing a ratio of carbon dioxide capacity within

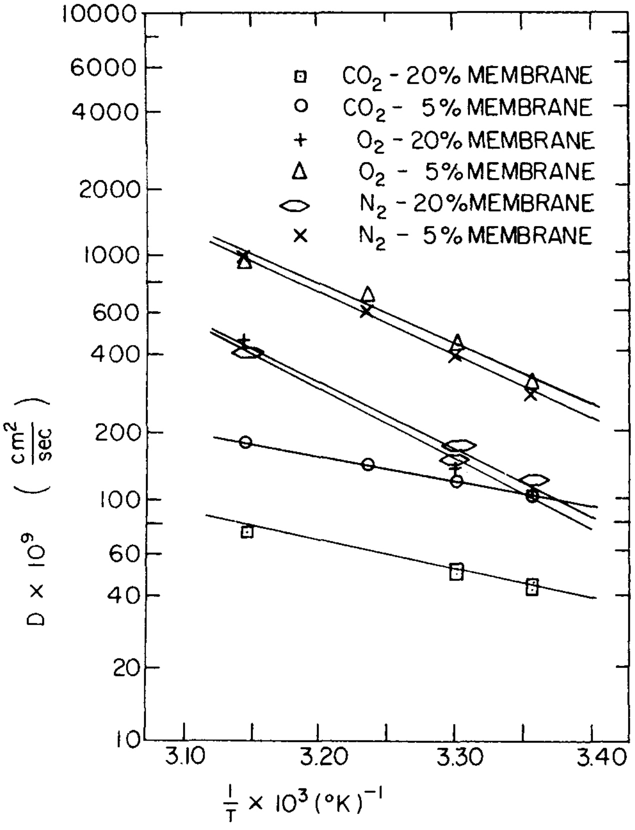

Fig. 4. Diffusion coefficients versus temperature, (*PEI/PVB* = 2).

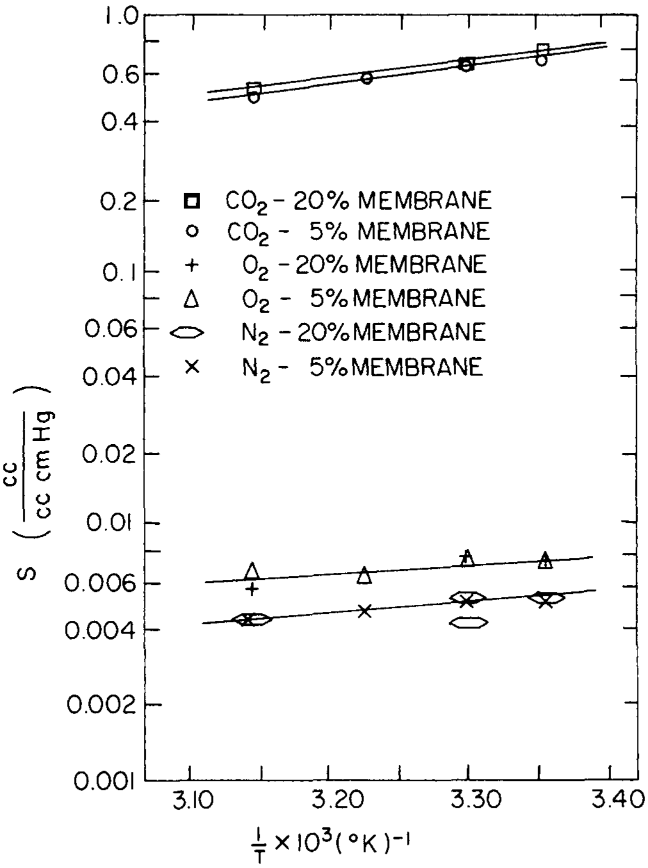

Fig. 5. Solubility versus temperature, (*PEI/PVB* = 2).

TABLE 2. ACTIVATION ENERGIES FOR DIFFUSION, CAL./MOLE

Permeant	Casting solution % solids 5%	20%
CO_2	5,000	5,300
O_2	11,200	12,600
N_2	11,600	13,000

TABLE 3. MEMBRANE WATER CONTENT

(20% solids, 2:1 PEI/PVB ratio)

% Relative humidity	Water content, g. H_2O/g. dry membrane
100	1.064
75	0.328
50	0.19
0	0.0

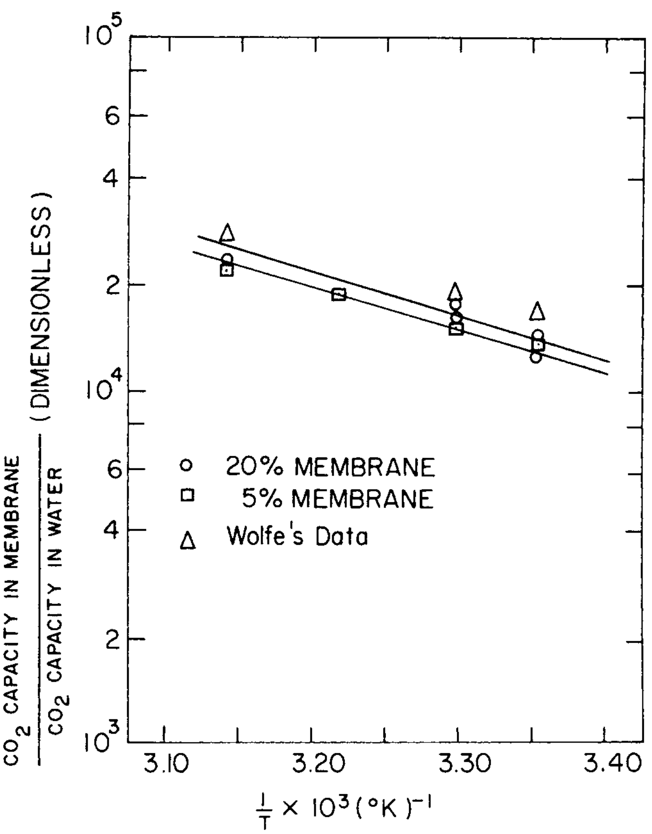

Fig. 6. Membrane capacity for CO_2 versus temperature, (PEI/PVB = 2).

the membrane to its capacity in water as a function of temperature is additional evidence for this equilibrium chemical reaction. The capacity ratio shown in Figure 6 may be taken as the equilibrium constant for the second chemical reaction. This equilibrium constant is seen to be extremely large, as should be expected.

In the case where diffusion takes place accompanied by a chemical reaction which immobilizes the diffusing species, Crank (*11*) has pointed out that the measured diffusion coefficient (in the case where the reaction is reversible first order) can be given by

$$D_m = \frac{D}{\alpha + 1} \tag{7}$$

Thus, the measured value for activation energy for diffusion really consists of two parts. The measured activation energy is equal to the difference between the actual activation energy for diffusion and the activation energy for the chemical reaction that immobilizes the diffusing species. If it is assumed that the actual activation energy for diffusion for carbon dioxide is of the same order as that for O_2 and N_2, then the apparent activation energy for the chemical reaction which immobilizes the carbon dioxide must be of the order of 6 kcal./mole, a not unreasonable value.

Effect of Casting Solution Composition

An examination of Figures 4 and 5 indicates that as the percent solids in the casting solution decreases, the diffusion coefficient for carbon dioxide, O_2, and N_2 increases, while the solubility is essentially unaffected. This increase in diffusion coefficient with a decrease in solids content may be attributed to the effect of different casting solutions on the density of the membranes obtained. Table 4 shows that as the solids content of the casting solution decreases the density of the membrane obtained also decreases. The table also shows the calculated density of a membrane made from a hypothetical 100% solids casting solution. This density effect is probably due to the fact that cross linking occurs while the solvent is evaporating. Thus, for the lower solids content casting solutions, a rigid three-dimensional structure forms which probably entraps less solute material than would the higher solids casting solutions. Thus, there is less retardation to diffusion in the former case than in the latter case, leading to a higher diffusivity.

The change in membrane transport properties as the PEI to PVB ratio is varied from 0 to 4 is shown in Table 5. In the case of carbon dioxide an increase in PEI/PVB ratio results in an increase in membrane permeability with a decrease in diffusion coefficient being compensated for by a large increase in membrane solubility. The increased membrane solubility is attributable to the chemical reaction in which the carbon dioxide is immobilized by the membrane imine groups. The decrease in diffusivity is attributable to an increase in membrane density. For PEI/PVB ratios greater than 2, the membranes that resulted were highly porous and nonselective.

For the case of O_2 and N_2 a change in PEI to PVB ratio results in very small changes in permeability, although there are slight changes in membrane diffusion coefficients and solubility for these two gases. The change in membrane diffusion coefficients for these gases follows the trend for carbon dioxide, which is to be expected. The data in this table came from measurements of a membrane made from a 20% solids content casting solution and indicates that the highest selectivity for carbon dioxide over O_2 and N_2 is obtained from the highest practical PEI/PVB ratio, 2:1.

The relationship of the selectivity for carbon dioxide over O_2 and N_2 to the PEI/PVB ratio is an indication of the

TABLE 4. MEMBRANE DENSITY (DRY) AS A FUNCTION OF CASTING SOLUTION (PEI/PVB RATIO = 2)

% Solids content to casting solution	Density (g./cc.)
100	1.080 (calculated)
20	0.877
16	0.862
10	0.845
5	0.836
2	0.833

TABLE 5. EFFECT OF PEI/PVB RATIO ON TRANSPORT PROPERTIES

(20% solids membrane, all measurements at 30°C.)

Property	PEI/PVB ratio 0	1	2	3	4
P_{CO_2} (cc.)(cm.)/(sq. cm.)(sec.)(cm. Hg × 10^9)	1.21	12.48	34.4	1070.0	5870.0
P_{O_2}	1.17	0.91	1.13	1420.0	6910.0
P_{N_2}	0.083	0.501	0.746	—	—
P_{CO_2}/P_{O_2}	1.03	13.7	30.4	0.75	0.86
D_{CO_2} (sq. cm./sec. × 10^9)	154.0	26.4	51.0	—	—
D_{O_2}	238.9	117.0	156.2	—	—
D_{N_2}	170.7	114.1	144.1	—	—
S_{CO_2} [cc./(cc.)(cm. Hg × 10^3]	7.9	473.0	675.0	—	—
S_{O_2}	4.90	7.78	7.19	—	—
S_{N_2}	0.486	4.40	5.21	—	—

TABLE 6. EFFECT OF RELATIVE HUMIDITY ON PERMEABILITY

(20% solids membrane, 2:1 PEI/PVB ratio, measurements at 30°C.)

% Relative humidity	P[(cc.)(cm.)/(sq. cm.)(sec.)(cm. Hg $\times 10^9$)]		
	CO_2	O_2	N_2
100	34.40	1.130	0.746
75	3.32	0.606	0.268
50	0.87	—	—
0	0.084	0.069	0.069

active role the imine groups play in this process. Since distilled water, due to its high carbon dioxide solubility, gives a selectivity ratio (CO_2/O_2) of about 20, one might argue that perhaps the water is responsible for the observed effects. Since the introduction of PEI essentially affects only the carbon dioxide permeability and not the O_2 or N_2 permeability, this is clearly not the case.

In a number of experiments lithium chloride was incorporated in the casting solution with the idea that after the membrane is made, it could be leached out and thus increase the porosity of the membrane. Lithium chloride contents used varied from 0.5 to 2.0% by weight. The results indicated that for those membranes in which significant changes in permeability were obtained (the membranes in which the lithium chloride affected the membrane permeability), the membranes produced were porous and nonselective. For this reason the use of lithium chloride additive was abandoned.

Effect of Relative Humidity

The permeability and selectivity of the membrane for carbon dioxide is strongly dependent on the relative humidity of the gas, as may be seen in Table 6 which presents data for a membrane made from a 20% solids content casting solution with a 2:1 PEI/PVB ratio with measurements taken at 30°C. For this system it is seen that when the relative humidity of the gas drops from 100 to 75%, the carbon dioxide permeability drops by a factor of 10, while the O_2 permeability drops by a factor of about 2, and the N_2 permeability by a factor of about 3. As has been pointed out, the membrane water content is highly dependent on the relative humidity of the gas. As water is removed from the membrane, the membrane shrinks in size and becomes stiffer. The additional stiffness is a result of the fact that the water acts as a plasticizer. Both the shrinkage and the stiffening lead to more resistance to transport and thus a decrease in diffusivity and permeability. The larger the diffusing molecule, the greater this effect would be. Thus, carbon dioxide would be more affected than either O_2 or N_2.

In the case of carbon dioxide there is an additional effect. The reaction and immobilization of carbon dioxide by the active groups in the membrane depend on the presence of water. A decrease in water content of the membrane would decrease the solubility of carbon dioxide in the membrane and thus lead to a lower permeability. Thus, the permeability for carbon dioxide drops faster than the permeability of O_2 and N_2 when the water content of the membranes is decreased.

CONCLUSIONS

The most important conclusion that can be derived from this work is that it is possible to make a membrane with good physical properties which will allow the selective permeation of carbon dioxide over O_2 and N_2 in ratios of the order of 30:1 or greater. This can be compared to typical selectivity ratios for inert membrane systems of the order of 4:1 or 5:1. This greatly increased selectivity for carbon dioxide is attributable to the increased solubility of carbon dioxide with the imine groups in the membrane. The possible use for such a membrane system for applications in which the concentration of carbon dioxide and other acidic gases is required is obvious.

Systems have been proposed in which several gas permeation stages would be used to remove carbon dioxide from air in such enclosed environments as submarines. Clearly, the highly selective membrane described in this report could make such a system considerably more simple and efficient than is possible with membranes commercially available at present. It is also likely that such a membrane could have a profound effect on improving the efficiency of membrane blood oxygenators when present mixing problems in such devices are solved.

ACKNOWLEDGMENT

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NOTATION

A = membrane area, sq.cm.
D = actual diffusion coefficient, sq.cm./sec.
D_m = measured diffusion coefficient, sq.cm./sec.
L = membrane thickness, cm.
P = permeability coefficient, cc.-cm./(sq.cm.)(sec.)(cm. Hg)
P_d = average driving force for permeation, cm. Hg
T = system temperature, °K.
V_c = receiving chamber volume, cc.
α = equilibrium constant for the chemical reaction, dimensionless
ΔP = change in pressure of receiving chamber in Δt sec., cm. Hg
S = solubility coefficient, cc./(cc.-cm. Hg)
θ = characteristic time lag, sec.

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