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# Permeation of Permanent Gases through Liquid Membranes

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## Abstract

The permeation of the permanent gases, He, $O_2$, $CO_2$, and $N_2$, through liquid membranes was investigated by two experimental methods. The first procedure utilized the simultaneous counterdiffusion of two pure gases through an aqueous-surfactant bubble membrane according to the technique developed by Cook. In the second, the transfer rate of a single pure gas was measured by utilizing a spherical soap bubble. Comparison of the data obtained from the two different tests indicated that these gas–liquid systems behaved ideally. That is, there were no observed interactions for the binary mixtures which could not be predicted from the behavior of the pure components. Finally, nonaqueous, silicone oil membranes were investigated as potential separative barriers. These oil films yielded the same separation factors as previously reported for silicone rubber membranes used in the separation of binary gas mixtures.

## INTRODUCTION

Cook and Tock (*1*, *2*) reported extensive data on the permeability of aqueous membranes to several permanent gases and speculated on the potential of liquid membranes as separative barriers for gas mixtures. The published diffusivities and separation factors were calculated from experimental information based on the movement of a soap bubble along a graduated buret. This technique was developed by Cook and requires that two dissimilar gases be positioned on each side of the liquid film. The unequal counterdiffusion rates of the two gases produce the bubble's movement for the closed system. This provided the desired information about the overall separation factor for the gas pair. However, the calculated diffusivity for each pure gas was questionable due to the presence of the second gas. To confirm unicomponent predictions obtained from the binary system, an experiment utilizing only a single pure gas was needed but never developed.

Also, Cook investigated only aqueous membranes which contained various surfactants. It was observed that the presence of the surfactant affected the calculated pure gas permeation constants only slightly, while the separation factor appeared to be due almost exclusively to the solubility differences of the gases in the pure liquid water. In the future selection of potential liquid membrane barriers, it would be useful to know whether or not this dependence of the overall separation on gas solubility remained predominant.

For these reasons a continuation of Cook's work appeared to be desirable. Therefore, an experiment was designed to study the relationships between the solubility and diffusive characteristics of permanent gases through liquid silicone oil films. To be consistent, the experimental approach used by Cook was followed as closely as possible. In addition, a second experimental procedure was developed to investigate the permeability of a single pure gas through a liquid membrane. Information gathered by the second procedure would then be compared with the binary gas data to reveal any gas–gas or gas–liquid interactions which had occurred.

## THEORETICAL

The theoretical derivations for predicting gas diffusivities and separation factors based on the movement of a bubble membrane in a calibrated buret have been developed by Cook et al. (*1*, *2*) along with the experimental technique. For a single pure gas permeability determination the failure of the liquid membrane to support a pressure drop severely restricted the experimental possibilities. The procedure utilized in this study was to place the pure gas under investigation on each side of a spherical bubble. In this arrangement the surface tension in the liquid film provided the required pressure drop across the bubble membrane (*3*, *4*).

The Laplace equation for a thin spherical bubble having two liquid–

gas interfaces is written as

$$(P_1 - P_2) = 3.0 \times 10^{-5}\left(\frac{\gamma}{R}\right) \tag{1}$$

The pressure drop across the bubble membrane is also used to determine the permeability coefficient *K*. *K* is defined as

$$K \equiv JL/(P_1 - P_2) \tag{2}$$

Since the surface tension acts to contract the bubble as the pure gas permeates it, the volumetric flux rate, *J*, can be related to the rate of change in the bubble radius.

$$J = C\frac{dR}{dt} \tag{3}$$

In this instance *C* is a constant coefficient for converting the volume change for the test to standard *T* and *P* conditions. Equation (3) also assumes that the bubble is large compared to the thickness of the film, and that for small volume changes the surface area of the bubble remains essentially constant. Under these conditions Eq. (1) and Eq. (3) are substituted into Eq. (2) and integration performed on *R* and *t*.

$$K = (CL)\left(\frac{dR}{dt}\right)\Big/\left[3.0 \times 10^{-4}\left(\frac{\gamma}{R}\right)\right] \tag{4}$$

At $t = 0$, $R = R_1$, and $t = t_f$, $R = R_f$, then

$$K = \left(\frac{C_0 L}{\gamma}\right)\left(\frac{R_1^{\,2} - R_f^{\,2}}{t_f}\right) \tag{5}$$

where $C_0 = 6535P/T$.

For a pure component system, the permeability coefficient is now a function of time, bubble radius, membrane thickness, surface tension, and the temperature and pressure for the system. All are measureable quantities and for reasonably short time periods controllable variables.

## DISCUSSION OF RESULTS—SILICONE OIL MEMBRANES

For the nonaqueous, silicone oil membranes, two GE, electrical grade silicone fluids numbered SE-85(50) and SF-97(20) were utilized. They differed only by their molecular weights and hence viscosities. Quite early in the experimental process it was observed that these liquids would not form films with sufficient stability to permit complete data collection. Therefore, a modification of Cook's procedure was required. It was observed that a small amount of surfactant (ivory solution) would increase membrane lifetime when added to the bulk silicone oil. Also, it was accidentally discovered that when the test gases were saturated with water vapor, the films were even more stable. The results for the silicone oil membranes are shown in Tables 1 and 2.

According to the data, of the four gases tested, $CO_2$ was the most permeable followed by helium, oxygen, and nitrogen in that order. This is essentially the same order reported by Robb (*5*) for silicone rubber

TABLE 1

Experimental Binary Gas Permeation Parameters for GE SF-85(50) + Ivory Solution

| | Calculated from initial slope | | | Calculated by curve fit | | |
|---|---|---|---|---|---|---|
| System A–B | Alpha | $K_A \times 10^9$ | $K_B \times 10^9$ | Alpha | $K_A \times 10^9$ | $K_B \times 10^9$ |
| He, $O_2$ | 2.11 | 41.1 | 19.6 | 1.70 | 54.9 | 32.3 |
| $CO_2$, $O_2$ | 3.71 | 40.7 | 11.0 | 3.71 | 41.2 | 11.1 |
| $CO_2$, $O_2$ | 2.75 | 117.5 | 42.6 | 3.00 | 75.2 | 25.0 |
| $CO_2$, $O_2$ | 4.55 | 76.2 | 16.7 | 4.66 | 73.2 | 15.7 |
| $CO_2$, $O_2(H_2O)$[a] | 2.54 | 124.0 | 48.8 | 2.68 | 128.9 | 48.2 |
| $CO_2$, He | 3.35 | 42.4 | 12.6 | 4.57 | 80.2 | 17.5 |
| $CO_2$, He$(H_2O)$[a] | 3.62 | 172.5 | 47.6 | 4.16 | 195.5 | 47.0 |
| $CO_2$, $N_2$ | 4.58 | 95.7 | 20.9 | 5.04 | 85.5 | 17.0 |
| $CO_2$, $N_2$ | 4.28 | 77.6 | 18.1 | 4.44 | 57.9 | 13.1 |
| $CO_2$, $N_2(H_2O)$[a] | 3.77 | 128.2 | 37.7 | 3.89 | 242.7 | 63.3 |
| $O_2$, $N_2$ | 1.79 | 85.7 | 48.0 | 1.84 | 75.5 | 40.9 |
| $O_2$, $N_2$ | 1.90 | 43.7 | 23.0 | 2.04 | 26.2 | 12.9 |
| He, $N_2$ | 1.07 | 53.5 | 49.9 | 1.15 | 20.0 | 17.3 |

[a] Gases were saturated with water vapor.

TABLE 2

Experimental Binary Gas Permeation Parameters for GE SF-97(20) + Ivory Solution

| | Calculated from initial slope | | | Calculated by curve fit | | |
|---|---|---|---|---|---|---|
| System A–B | Alpha | $K_A \times 10^9$ | $K_B \times 10^9$ | Alpha | $K_A \times 10^9$ | $K_B \times 10^9$ |
| $CO_2$, $O_2$ | 2.25 | 76.0 | 17.5 | 4.51 | 56.7 | 12.6 |
| $CO_2$, $N_2$ | 4.41 | 75.9 | 17.1 | 4.87 | 74.9 | 15.4 |
| $O_2$, $N_2$ | 1.95 | 51.9 | 26.6 | 2.04 | 31.8 | 15.6 |

TABLE 3

Robb's (S) Solubilities and Diffusion Rates of Gases in Silicon Rubber at 28 °C

| Gas | $K \times 10^{9a}$ | $D \times 10^6$ | $S$ |
|---|---|---|---|
| $CO_2$ | $323^b$ | 11 | 2.2 |
| $O_2$ | $62^c$ | 16 | 0.31 |
| He | 35.5 | 60 | 0.045 |
| $N_2$ | 28.7 | 15 | 0.15 |

[a] $K = DS/75$.

[b] McGregor (*6*) reported $CO_2$ solubility in dimethyl silicone fluids equal to one-half that given by Robb.

[c] Cannon, St. Pierre, and Miller (*7*) have measured an $O_2$ solubility in dimethyl silicone oil equal to one-half that reported by Robb.

membranes as shown in Table 3. The difference between the two is the increased permeability of the helium through the silicone oil as opposed to the rubber. This was attributed to the presence of the surfactant and attendant water, both of which would not affect the thicker rubber membranes. Generally speaking then, the gas permeabilities for both the silicone oil and rubber membranes were identical when they were normalized for thickness, pressure drop, area, and the flow rates corrected to standard conditions. This implied that the silicone oil membranes would exhibit separation factors of the same order of magnitude as the silicone rubber. They did indeed show this.

Another significant aspect of the data shown in Table 1 is the wide variation for identical gas pairs on duplicate runs. This was attributed to changes in the thickness of the silicone oil membrane. Unlike the aqueous-surfactant membranes, the liquid silicone films were relatively unstable. Upon initial formation they were at maximum thickness, and they became progressively thinner with time and accumulated drainage. Thus unlike Cook who measured his film thicknesses and established that they remained relatively constant, this study assumed a constant thickness, which in fact varied. Thus data collected soon after film formation produced smaller calculated permeability coefficients than that collected after a significant time delay following formation.

Finally, the data in Table 1 show a most interesting effect created by the presence of water vapor in the system. In every case the water increased the permeability significantly. Qualitative tests indicated that this was possibly due to the formation of a layered liquid membrane. Since water and silicone are immisible, it was theorized that the surfactant may have introduced this layered effect so that a water-rich phase was in contact with the gas phases, and the silicone oil-rich phase was sandwiched in between. The increased solubility of the gases in the water as compared to silicone oil would then tend to lower the absorption barrier prior to their transfer. This would increase permeability according to the $K = DS$ relationship. The creation of such anisotropic membranes could be of significance for biological studies.

## UNICOMPONENT SOAP BUBBLE EXPERIMENTS

The pure gas experiments using spherical soap bubbles appeared to give reasonable results once the technique had been developed. For this study it was imperative that the test gas be clean to insure a lifetime for a soap bubble in excess of 20 min. Even with clean, filtered gases, drainage due to gravity tended to distort the bubble from its spherical shape and cause a variation in the wall thickness. Table 4 shows the results of the tests, together with the predicted results of Cook for other aqueous-surfactant solutions. As shown, there is good agreement between the two studies. This implies that for these permanent gases behavior is ideal, and that there is no gas–gas or gas–liquid interaction. Thus the mixture behavior can be predicted from the pure gas behavior of the constituents and vice versa.

An interesting aspect of the experiment not shown in Table 4 was the behavior of the carbon dioxide. This gas could not be run since a bubble could not be formed for sufficient time to collect data. Either the $CO_2$ was reacting chemically or its permeation rate was so rapid that instability was introduced and collapsed the bubble.

## CONCLUSIONS

Data collected in this study confirmed the supposition that the solubility of the gases in the bulk fluid of the liquid membrane determined the

TABLE 4

Experimental Single Gas Permeation Coefficients for Soap Bubbles Compared with Cook's Predicted Values

| Gas | This study, $K \times 10^9$ (av) | Cook's study, $K \times 10^9$ (av) |
|---|---|---|
| He | $1.20 \pm 0.4$ | 0.722 |
| $O_2$ | $0.99 \pm 0.4$ | 0.571 |
| $N_2$ | $0.35 \pm 0.05$ | 0.220 |

separation factor. Moreover, based on the bubble experiments with a single gas, it was determined that for the permanent gases investigated their behavior was ideal.

The introduction of water vapor was found to stabilize the silicone oil membranes which had been treated with a surfactant. This was believed to be due to the creation of a multilayered membrane which increased permeability but did not change selectivity.

Finally, while this study once again indicated that liquid membranes can effect separations of mixtures of permanent gases, it also reinforced the fact that the major deterrent to the use of liquid films for this purpose is their highly fragile nature. Future research should look into the development of more stable liquid membranes. In this regard the permeability work by Van Amerongen (*8*) on melts of gutta percha and Nielsen (*9*) on polyethylene melts takes on renewed interest. The creation of anizotropic liquid membranes could also lead to some interesting performances and to some applications to biological systems.

## SYMBOLS

| | |
|---|---|
| $P_1$ | pressure inside soap bubble (cm Hg) |
| $P_2$ | pressure outside soap bubble (cm Hg) |
| $\gamma$ | surface tension of soap bubble (dynes/cm) |
| $R$ | bubble radius (cm) |
| $L$ | bubble wall thickness (cm) |
| $K$ | permeability coefficient (std cc cm/cm$^2$, cm Hg, sec) |
| $J$ | volumetric flux rate (cm$^3$/sec cm$^2$) |
| $t$ | time (sec) |

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