THIN SILICONE MEMBRANES—
THEIR PERMEATION PROPERTIES AND SOME APPLICATIONS

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INTRODUCTION

While the permeation of gases through solid materials is often a nuisance and sometimes a hazard, in recent years several useful applications have been found for this phenomenon. For example, H_2 is purified by diffusion through Pd-Ag foils, O_2 partial pressures are measured in instruments dependent on O_2 permeating through a plastic membrane, and artificial lungs based on permeation of O_2 and CO_2 through thin polymeric membranes are being developed. These applications are only the beginning, for recent advances in membrane technology portend uses as far afield as water desalination by reverse osmosis and the separation of azeotropes by membrane perm-vaporation.

When one wishes to separate noncondensable gases by a membrane technique, his first consideration should be whether a silicone rubber membrane can be used. This stems from the unusually high permeability of silicone rubber, indicated in TABLE 1, a tabulation of O_2 permeabilities in various membranes.

TABLE 1

O_2 PERMEABILITIES IN VARIOUS POLYMERS

Polymer	$Pr_{O_2} \times 10^9$ $\left[\dfrac{cc\text{'s (RTP), cm}}{\text{sec, sq cm, cm Hg } \Delta P} \right]$
Dimethyl silicone rubber	60
Fluorosilicone	11
Nitrile silicone	8.5
Natural rubber	2.4
Ethyl cellulose	2.1
Polyethylene, low density	0.8
BPA polycarbonate	.16
Butyl rubber	.14
Polystyrene	.12
Polyethylene, high density	.1
Cellulose acetate	.08
Methyl cellulose	.07
Polyvinyl chloride	.014
Polyvinyl alcohol	.01
Nylon 6	.004
Polyvinylidene fluoride	.003
Mylar	.0019
Kel F (unplasticized)	.001
Vinylidene chloride—vinyl chloride	.0005
Teflon	.0004

This Table shows that not only standard dimethyl silicone rubber but also many silicone derivatives have O_2 permeabilities higher than even the most permeable nonsilicone plastics. In addition to high permeabilities, silicone rubber also has

useful selectivity; i.e., it allows certain gases to permeate faster than others. In fact, these properties suggested that, were it available in a 1-mil, hole-free film and in a form that could be packaged and supported against a high-pressure gradient, silicone rubber could compete with other methods for enriching or extracting certain gases. In addition, certain processes not heretofore possible would become feasible; for example, the creation of an artificial gill for humans.

A method to produce such membrane has been developed, and 1-mil hole-free silicone rubber, either free or bonded to a porous support cloth, is now available in limited quantity. In light of this availability, it is worthwhile to examine the permeation properties of silicone rubber in greater depth. In addition, the results of an experimental study of three possible applications of the membrane are herein presented; oxygen enrichment, air regeneration in an isolated chamber, and air regeneration underwater.

GAS PERMEABILITY IN SILICONE RUBBER

Experimental Procedure

The first published values for the permeability of ordinary gases in silicone rubber are those of Kammermeyer[1], reported in 1957. Barrer et al.[2,3] reported permeabilities of C_4 and C_5 hydrocarbons in silicone rubber, and they measured solubilities and diffusion rates of these vapors as well. Other data on the permeability of silicones are given by Roberts and Kammermeyer.[4]

Permeabilities measured in this laboratory show no disagreement with previously published values. In this section, new measurements are reported for a variety of gases over a very wide range of parameters such as film thickness, temperature, pressure, gas composition, etc.; in addition, measurements of diffusion rates and solubilities in silicone rubber by the "time-lag" method are reported for several gases.

Permeability constants measured for many gases and vapors on a sample of filled dimethyl silicone rubber film are given in TABLE 2. This particular silicone rubber consisted of dimethyl siloxane plus 33% by weight silica filler. The meas-

TABLE 2
GAS PERMEABILITIES IN DIMETHYL-SILICONE RUBBER (25%)

Gas	$Pr \times 10^9$ $\left[\dfrac{\text{cc gas (RTP) cm}}{\text{sec, sq cm, cm Hg } \Delta P}\right]$	Gas	$Pr \times 10^9$ $\left[\dfrac{\text{cc gas (RTP) cm}}{\text{sec, sq cm, cm Hg } \Delta P}\right]$
H_2	65	C_2H_4	135
He	35	C_2H_2	2640
NH_3	590	C_3H_8	410
H_2O	3600	$n-C_4H_{10}$	900
CO	34	$n-C_5H_{12}$	2000
N_2	28	$n-C_6H_{14}$	940
NO	60	$n-C_8H_{18}$	860
O_2	60	$n-C_{10}H_{22}$	430
H_2S	1000	HCHO	1110
Ar	60	CH_3OH	1390
CO_2	325	$COCl_2$	1500
N_2O	435	Acetone	586
NO_2	760	Pyridine	1910
SO_2	1500	Benzene	1080
CS_2	9000	Phenol	2100
CH_4	95	Toluene	913
C_2H_6	250		

urements were made in a conventional two-bulb apparatus that could be evacuated initially to less than 10^{-3} mm Hg pressure. The silicone membrane was supported on a porous paper and screen, and the thickness of the membrane was determined from the weight of a given area of membrane.

Following evacuation of both the high- and low-pressure sides of the permeability cell, gas was admitted to the high-pressure side from a container of gas at known pressure and volume. Permeability rates were usually measured with only a few centimeters of mercury pressure of the specific gas on the high-pressure side. For the "noncondensable" gases, a McLeod gauge was used to measure the pressure buildup on the low-pressure side of the membrane. For the condensable hydrocarbons, a mercury manometer and cathetometer were used, the vapor pressure on the high-pressure side always being kept below the saturated vapor pressure. Water permeation rate was measured by the weight loss of a membrane-covered cup of water which was kept in a dry environment.

Permeation rates are given at 25°C in terms of cc's of an ideal gas or vapor measured at one atm and 25°C. For condensable vapors, this is an artificial volume that might cause confusion if not realized.

Measurement of Gas Solubility and Diffusion in Coefficient

The data in TABLE 2 support the hypothesis that permeation of polymeric membranes does not occur by leakage through small holes in the membrane. It will be noted, for example, that helium is one of the least permeable gases in spite of its having the smallest molecular diameter.

Carbon dioxide is seen to permeate about ten times as fast as helium, and the aliphatic hydrocarbons are seen to peak at C_5, with lower permeation rates being measured for both shorter and longer hydrocarbon molecules. This order of permeabilities for various gases in silicone rubber is consistent with permeation in other polymers. It was first proposed by Graham in 1866, and in greater detail by Wroblewski in 1879, that the permeability rate is really a function of two more basic properties: the solubility (S) of the gas in the polymer and the rate of diffusion (D) of this dissolved gas in the polymer. More specifically, it was proposed that the permeability constant (Pr) was really the product of the diffusion rate and solubility; i.e., Pr = D × S.

Daynes[5] showed that D and S could be determined from permeability measurements by the "time-lag" method, provided Fick's and Henry's laws apply. By use of this method of measurement, diffusion coefficients and solubilities were

TABLE 3

SOLUBILITIES AND DIFFUSION RATES OF GASES IN SILICONE RUBBER

Gas	Temp (°C)	Pr × 10^9	$D \times 10^6$ $\left(\dfrac{cm^2}{sec}\right)$	$S\left[\dfrac{cc(RTP)}{cc,atm}\right]$
He	28.0	35.5	60	0.045
H₂	27.5	66	43	.12
CH₄	27.5	94	12.7	.57
N₂	28	28.7	15	.15
O₂	27.4	62	16	.31
Ar	27.5	61.3	14	.33
CO₂	27.6	323	11	2.2
C₄H₁₀	26	~1000	~5	15

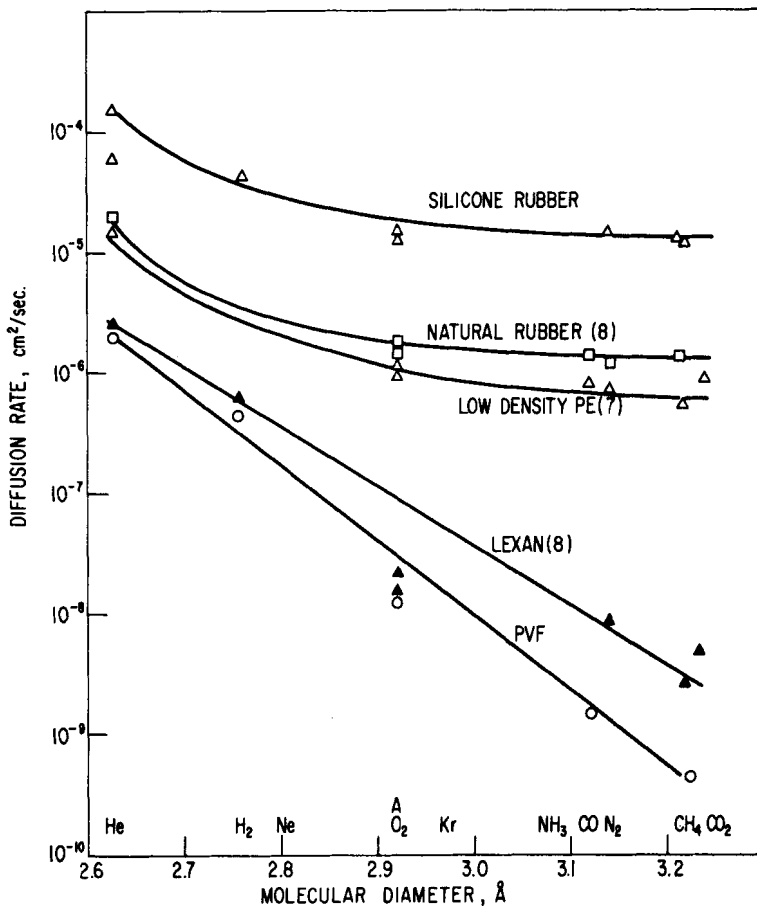NOTE: $Pr = \dfrac{D \times S}{75 \text{ cm Hg/atm}}$

FIGURE 1.   Diffusion rates of dissolved gases in polymers.

obtained for various gases and vapors in silicone rubber. These data are given in TABLE 3. The diffusion coefficients and gas solubilities are also shown in FIG-URES 1 and 2 along with comparable data for other polymers.

It is seen that the solubilities measured are very comparable to those reported for other polymers, and they are also comparable to gas solubilities in many organic liquids. As Hildebrand and Scott[9] point out, the solubilities increase exponentially with the Lennard-Jones constant for the gases, this constant being closely approximated by the normal boiling point of the gas in degrees Kelvin. On the other hand, diffusion rates in silicone rubber are seen to be almost an order of magnitude higher than diffusion rates for the same gases in the most permeable hydrocarbon polymers. Therefore, the unusually high permeabilities in silicone rubber are mainly due to the high rate of diffusion of the dissolved gases. This property of silicone rubber is a direct result of the greater flexibility or mobility of the Si-O bond as compared to the C-C or C=C bond characteristic of the polymeric backbone of natural rubber.
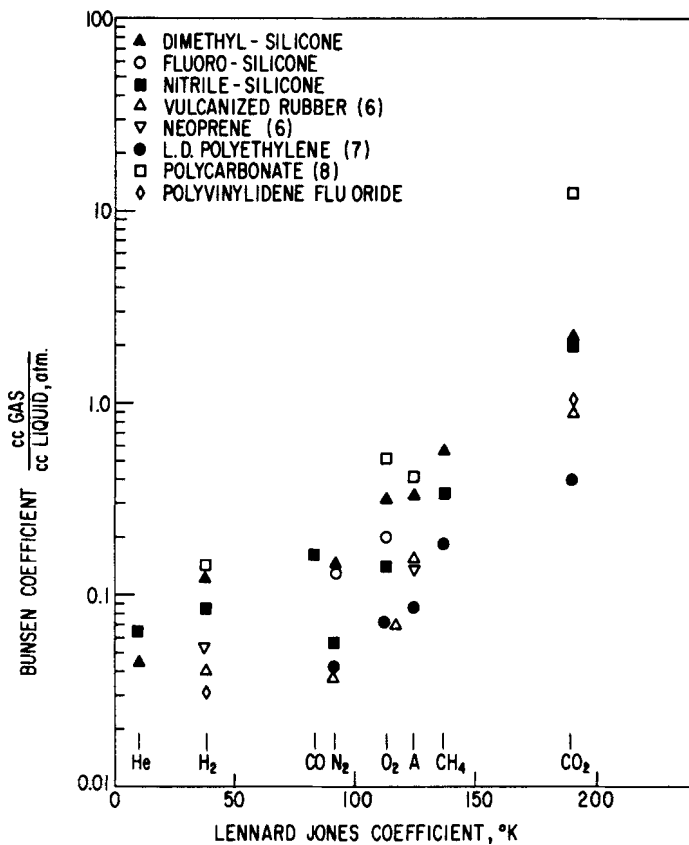
FIGURE 2. Gas solubilities in polymers.

Direct measurements of gas solubilities in silicone materials with a sorption balance agree reasonably with the solubility values obtained indirectly by the "time-lag" method. McGregor[10] has reported solubilities for O_2 and N_2 in dimethyl silicone fluids essentially equal to those reported here, and a value for CO_2 one-half that reported here. Also, Cannon, St. Pierre, and Miller[11] have measured an O_2 solubility in dimethyl silicone oil equal to one-half that reported here for silicone rubber.

No direct diffusion measurements of gases in silicone rubber have been reported. However, it is interesting to compare the diffusion rates of dissolved gas molecules with the self-diffusion of silicone fluids reported by McCall, Anderson, and Huggins.[12] Using the NMR spin-echo technique, they determined self-diffusion coefficients for siloxane fluids of varying molecular weight. These data are given in FIGURE 3. Note that O_2, N_2, and CO_2 have diffusion coefficients in silicone rubber approximately equal to the self-diffusion coefficient of a dimethyl silicone molecule containing three Si atoms. One could interpret this to indicate that an opening in the polymer sufficiently large to permit a gas molecule to jump from one hole to another would require the motion of a silicone chain segment of the order of three monomer units in length.

Effect of Pressure, Membrane Thickness, and Gas Flux on Permeability

Permeability measurements for O_2, N_2, and CO_2 have been made with pressure differences across the membrane ranging from 0.2–500 psi pressure. Within the accuracy of the experiments, no change in permeation as a function of pressure has been detected. The ratios of permeabilities likewise remain constant to within $\pm 10\%$. This would indicate that Fick's law was certainly obeyed in these systems and that either the gases were not appreciably plasticizing the membrane or, if so, the diffusion rates in the plasticized and unplasticized membrane were the same. Since the diffusion rate of gases in unplasticized silicone rubber is very near that for gases in many liquids, it would not be surprising if plasticization caused little change in permeation.

Membrane thicknesses have been varied from 0.1 mil to 30 mils without showing any effect of thicknesses on permeability. This indicates that gas absorption and desorption at the membrane surfaces offer negligible resistance compared with gas diffusion through the membrane even for very thin membranes.

Actually, the highest flux through a membrane was obtained with 500 psi ΔP across a 1-mil membrane. With this pressure gradient, 0.25 cc CO_2 (NTP) permeated 1 cm^2 of membrane area per second. Furthermore, using the solubility
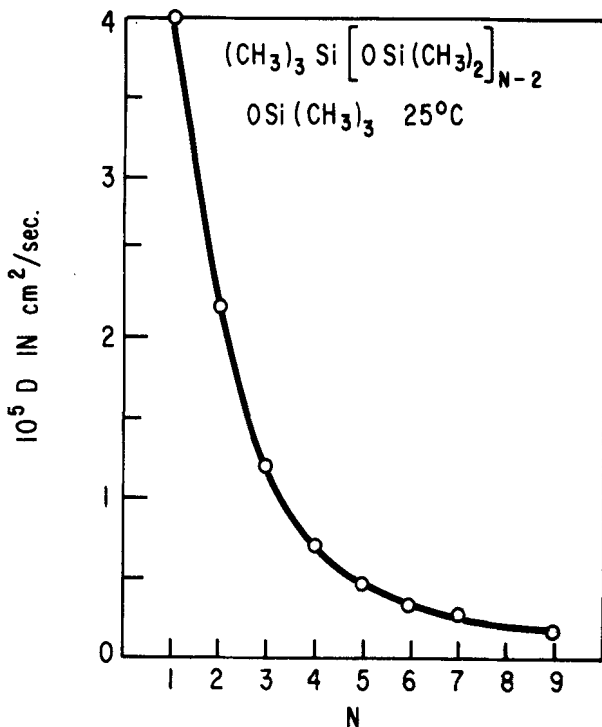

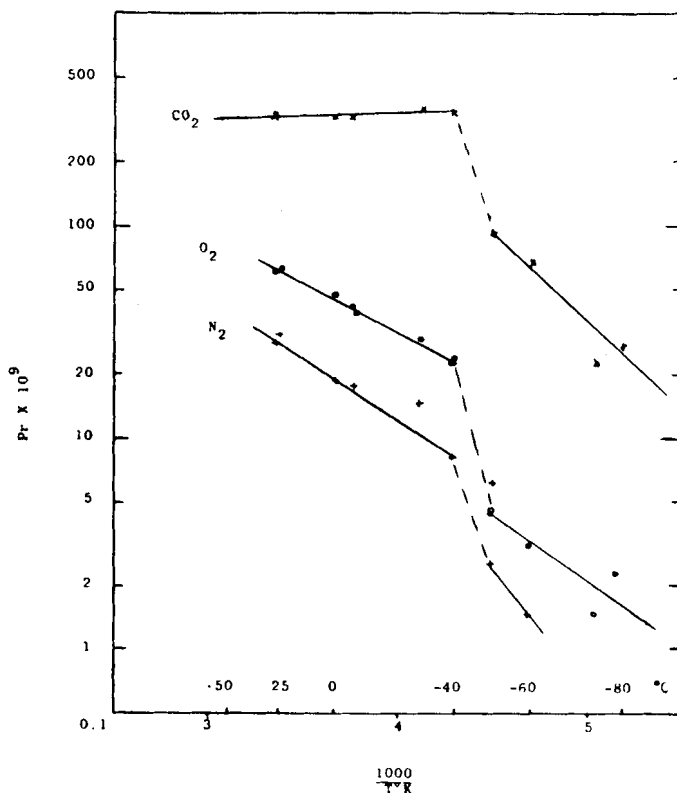FIGURE 3. Self-diffusion coefficients of siloxane fluids.

FIGURE 4. Effect of temperature on the permeation rate of dimethyl silicone rubber.

constant for CO_2 previously reported, one finds at this pressure that the membrane adjacent to the high-pressure gas contained 0.1 gram of CO_2 in solution per gram of silicone rubber. No nonlinear effect of this high flux was found on the permeability rate calculated from the experiment.

Temperature Effect on Permeability

The effect of temperature on the permeability of dimethyl silicone rubber is shown in FIGURE 4. Of particular interest is the small effect of temperature on Pr_{CO_2} as long as the silicone rubber is above its crystalline melting temperature of approximately $-40°C$. This results in a Pr_{CO_2} to Pr_{O_2} ratio of 16 at $-40°C$, which could be of value where high separation factors are required. In FIGURE 5, similar data are given for a silicone rubber specially modified for low temperature use. Permeabilities are higher at the low temperatures, since crystallization occurs to a much lesser extent in this material.

Values of diffusion rate and solubility in silicone rubber at low temperature are given in TABLE 4. These data show that the high CO_2 permeability at lower temperature is caused by a high CO_2 solubility. This greatly increased solubility of CO_2 compared with O_2 and N_2 is consistent with the much higher boiling point of CO_2 (at $-40°C$, a condensed state is being materially approached only by CO_2).

TABLE 4

EFFECT OF TEMPERATURE ON PR, D AND S IN SILICONE RUBBER

Gas	Temp (°C)	Pr × 10⁹	D × 10⁶	S
O_2	28	62	16	0.31
	−40	20	3.9	.39
	−75	0.74	0.0012	47
CO_2	28	323	11	2.2
	−40	293	2.7	8.2
	−75	22	0.0022	770

THE EFFECT OF FILLER CONTENT AND CROSSLINKING ON PERMEABILITY

Permeabilities were measured in dimethyl siloxanes containing from 0–60 w/o silica filler. Over this range of filler content, O_2 permeabilities only varied from 70 × 10⁻⁹ cc (RTP)/cm² sec cm Hg/cm to 40 × 10⁻⁹. This is consistent with the data of Gregory,[13] which showed that flake-type fillers appeared to have more effect than other fillers on permeability rates.
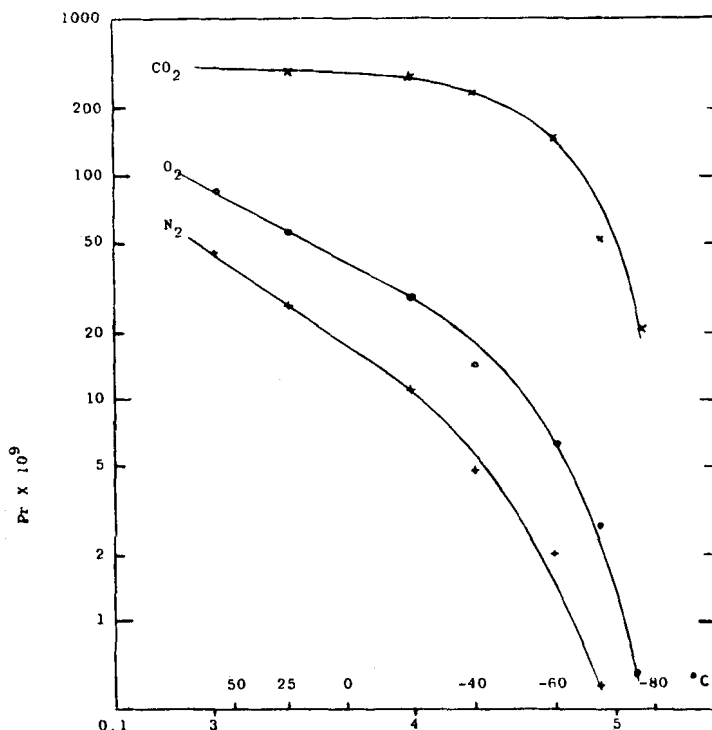

FIGURE 5. Effect of temperature on the permeation rate of a low-temperature silicone rubber.

Samples of silicone rubber containing a few tenths of a percent vinyl groups were irradiated to doses of 10^7, 3×10^7, $\times 10^8$ roentgen. Permeability data on these films are given in TABLE 5. At 10^8 r, the silicone rubber became fairly brittle, yet the permeability was reduced only a small amount. It is estimated that 10^8 r will form one crosslink every 50 monomer units. While this is sufficient to considerably change the gross mechanical properties of the rubber, it appears to have had little effect on the motion of small (ca. 3 monomer units long) segments of the silicone chain.

TABLE 5

EFFECT OF RADIATION ON PERMEABILITIES IN SILICONE RUBBER

Total Dose of Electrons (roentgens)	$Pr \times 10^9$ (25°C)		
	O_2	N_2	CO_2
0	57	27	285
10^7	51	23.5	275
3×10^7	51	23.5	295
10^8	46	21.5	260

PERMEABILITIES OF OTHER SILICONE POLYMERS

The previous data have pertained exclusively to dimethyl siloxane based polymers. Permeabilities of other siloxanes, for which some or all of the methyl groups on the siloxane have been replaced with other groups, are reported in TABLE 6. In general, the bulkier the groups attached to the silicon atom, the lower is the permeability observed. Diffusion and solubility data show that the gas solubilities are only slightly dependent on the siloxane composition, while the diffusion rates are considerably reduced when the methyl groups are replaced.

TABLE 6

GAS PERMEABILITIES OF CHEMICALLY MODIFIED SILOXANES

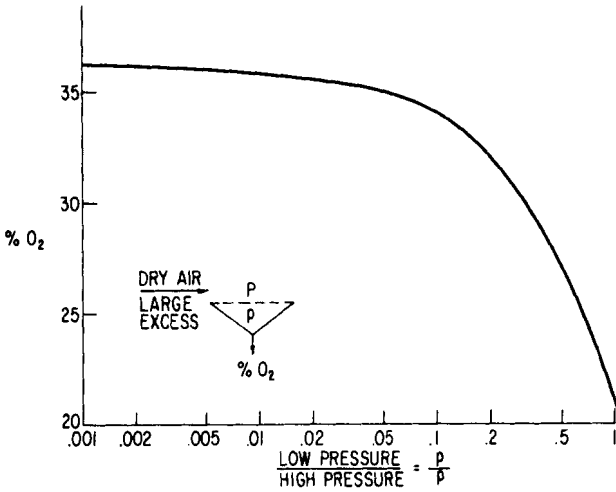| Composition of Side Groups on Silicone Atom	He	H_2	$Pr \times 10^9$ (25°C) O_2	N_2	CO_2
Dimethyl		65	60	28	325
5% Phenyl 95% Methyl			45	20.4	
20% Phenyl 80% Methyl		19.1	12.6	4.96	72.2
33% Phenyl 67% Methyl		7.74	4.45	1.42	29.5
50% Phenyl 50% Methyl		4.4	1.42	0.485	
67% Phenyl 33% Methyl		1.23	0.36	.081	1.9
80% Phenyl 20% Methyl		1.23	.21	.044	1.02
Nitrile silicone	8.6	12.3	8.5	3.3	67
Fluoro-silicone			11.4	4.9	

FIGURE 6.   Maximum O_2 enrichment with silicone rubber at various pressure ratios.
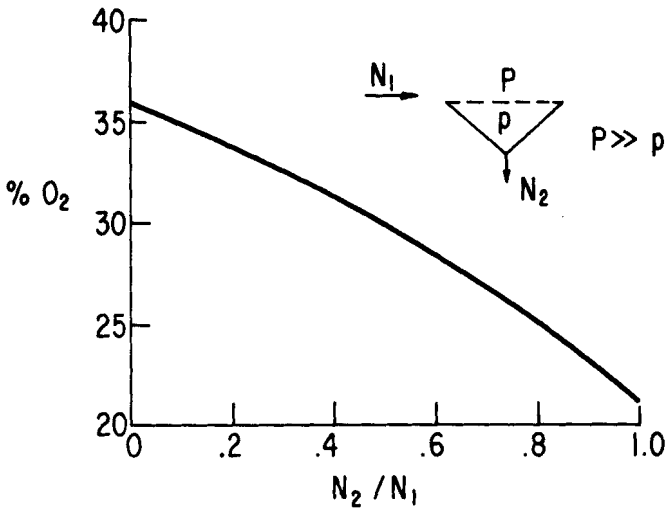

FIGURE 7. O_2 enrichment as a function of the fraction of air permeating.

APPLICATIONS FOR THIN SILICONE MEMBRANES

To illustrate some uses for thin, hole-free silicone rubber membrane, several devices built and tested at the General Electric Research and Development Center, K-1, will be described. It will be obvious that many other applications are also possible, but no attempt is made here to list all the uses or to describe all the experiments made. It should be realized that the same experiments could be carried out with thicker silicone membranes or less permeable polymers. However, the area of membrane required would be proportionately larger in every case, and this would increase both the cost and size of the device.

Membrane Oxygen Enricher

Since oxygen is 2.15 times as permeable as nitrogen in silicone rubber, oxygen-enriched (or oxygen-depleted) air may be produced by a membrane device. For example, if fresh dry air is continually supplied to the high-pressure side of a supported membrane, the air that permeates the membrane can be enriched to as high as 36% O_2 on the low-pressure side. The percentage of enrichment will depend on the high-to-low pressure ratio, as shown in FIGURE 6. Thus one may obtain any desired enrichment simply by controlling the pressure ratio across the membrane.

The degree of enrichment will depend also on the extent to which the high-pressure feed air is depleted in oxygen. In FIGURE 6, the amount of feed air is assumed to be sufficiently large so that no significant O_2 depletion occurs. Obviously this will not always be the case, and in FIGURE 7 the enrichment is given for a device with a very large pressure ratio, but for limited amounts of feed air.

CO_2 and H_2O, because of their high permeabilities, are also enriched in the permeated gas. Fortunately, the CO_2 concentration in normal air is so low that, even though it is enriched manyfold, its final concentration is only a fraction of a percent. Water vapor is a more serious problem since it may be present in humid air to 2% or 3%. Particularly at high-pressure ratios, the product gas obtained from humid air will contain a high percentage of water. Obviously, when dry air is available, this problem is eliminated. On the other hand, a number of other solutions are possible:

1. Water vapor permeating the membrane can be chemically adsorbed before reaching the compressor. This reduces the compressive work to enrich a given amount of air, but does require periodic adsorbent regeneration.
2. Water vapor and O_2-enriched air permeating a membrane can be compressed to atmospheric pressure, cooled to room temperature, and the condensed water collected and removed. This will produce a humid enriched air quite desirable for certain medical applications. This method requires that the compressor be able to compress a wet gas.
3. The incoming air can be dried by several methods. This eliminates the need to handle wet gases on the low-pressure side.

These are some of the methods by which water vapor can be controlled. Each method has advantages and disadvantages. The requirements of a given system will determine which method is best for that situation.

While the percentage of O_2-enrichment depends on the pressure ratio, the membrane area needed for a specific requirement is inversely proportional to the pressure difference (ΔP); i.e., P-p. To minimize membrane area, it is advantageous to operate at the highest possible pressure. On the other hand, this can be wasteful of compressive work, and so some compromise between membrane area and ΔP is usually made. One possibility is to set p at atmospheric pressure and to set P sufficiently high to give the desired pressure ratio. Unfortunately, in this case, it is not realistic for N_1 to be many times larger than N_2, and so O_2 depletion occurs on the high-pressure side and lowers the percentage of enrichment. Nevertheless, there are many circumstances where incoming gas compression is desirable, particularly if there are other requirements for the compressed air not permeating, or if an expansion turbine can be used to recover work from this high-pressure air.

One device, built as a prototype of an O_2-enricher (FIGURE 8), consists of a small fan blowing fresh air past a stack of porous plates. These are covered on both sides with 1-mil silicone rubber and joined to a common manifold. This, in
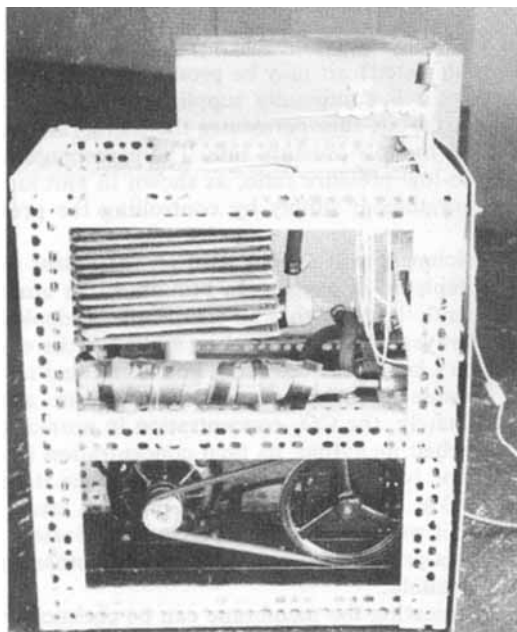
FIGURE 8.   Photograph of air enricher.

turn, is connected to a small vacuum pump or compressor that maintains a low pressure in the plates and manifold. The output of the compressor, filtered to remove droplets of water and oil coming from the compressor, is enriched to as high as 36% O_2, as measured on a calibrated Beckman O_2 analyzer and checked by mass spectrometry.

The effective area of the plates is approximately 8 ft², and the rate of flow of 36% O_2 air is 300 cc/min. This is equivalent to an O_2 permeation rate of

$$36 \times 10^{-9} \ \frac{\text{cc, cm}}{\text{sec, sq cm, cm Hg } \Delta P}$$

as compared with a value of 50×10^{-9} for this particular bare film. This reduction is mainly due to the blocking of the membrane by the supporting material, and is consistent with other data on supported membranes.

The measurement of the percentage of enrichment is a very severe test for holes in the membrane. For example, just one 1-mil hole per sq ft would result in the O_2 enrichment dropping from 36% to 34%.

It should be clear that the air permeating the membrane has been filtered to an extraordinary degree. The enriched air is thus free of dust, pollen, spores, bacteria, viruses, and essentially any component of the air that does not dissolve in silicone rubber. This is an advantage not found in an adsorption device for enriching air.

Oxygen enrichments higher than 36% can be obtained by adding a second stage of enrichment to the system. With a silicone rubber membrane it is possible to get 52% O_2 in two stages and 60% O_2 in three stages. The amount of membrane area and compressive work goes up sharply with the addition of

higher stages, and above 45% O_2 enrichment it is advantageous to use membranes with higher selectivities even at the expense of lower absolute permeation rates.

In a system in which the incoming air rate is limited, the gas not permeating the membrane is obviously depleted in H_2O, CO_2 and O_2. Thus one can use a membrane device to enrich an air stream in N_2. Such devices could be used to produce dry, O_2-depleted air continuously and would require no regeneration and charging of chemicals.

Membrane Air Regenerator

The ability of a membrane device to supply air filtered to an unusual extent suggests other uses for 1-mil silicone film. Two examples are (1) to supply air to germ-free animal colonies, and (2) to remove particulates such as radio-active fallout, germs, bacteria, or pollen from contaminated air. Certainly, this filtering can be done using a compressor either to push or to pull the air through the membrane, but equally interesting is the possibility of supplying filtered O_2 and removing CO_2 without a compressor. This is possible if one is willing to accept a slightly lower oxygen content and a higher carbon dioxide content in the breathing air.

Consider a man enclosed in a box covered with a film of thin, hole-free silicone rubber. If this box had a volume of 64 ft,[3] the man's metabolism would reduce the O_2 concentration about 1%/hr. However, as the O_2 content within the box drops below its concentration in the atmosphere, the O_2 partial pressure difference across the membrane will cause O_2 to permeate into the box. To maintain an O_2 percentage of 15% (equivalent to the O_2 partial pressure 8000 ft above sea level), a box containing a man would require 8.75 yd^2 of 1-mil silicone rubber membrane. This is slightly less than the area of five sides of a box four feet on edge. Increasing the area would, of course, raise the O_2 content reached at steady state.

Simultaneously, a man will also be producing CO_2, and if it were allowed to collect in the box, its concentration would rise approximately 1%/hr. However, within an hour the increase in CO_2 partial pressure in the contained atmosphere will give rise to an outward permeation rate equal to the man's rate of CO_2 generation. From this point on, the percentage of CO_2 in the box will remain constant. The initial rise in CO_2 concentration to 1%, it should be mentioned, is not harmful to man or to an animal. Even combined with 15% O_2, it would only be noticeable to a person doing moderate exercise. It is indeed fortunate that CO_2 is five times more permeable than O_2, for the body can tolerate greater decreases in O_2 partial pressure than it can increases in CO_2 partial pressure.

The man in the cell also produces water vapor by exhalation and evaporation. This amounts to about 1000 g/day and, if allowed to collect, would soon bring the relative humidity in the box to 100%. However, the silicone film allows this water to permeate to the outside air; for a surface area of 8.75 yd,^{2} the relative humidity inside the cell at steady state would be 15% higher than that outside.

The design of this air regenerator does not require the membrane to cover the outer surface of the box. It may be desirable to have the membrane filter a substantial distance from the living quarters, as shown in FIGURE 9, which is a conceptual plan for a fallout shelter. In this design, natural convection is used to circulate the enclosed air up a chimney, past the membrane where the air is cooled, and then back down to the living quarters. This natural convection depends on the living area being several degrees warmer than the outside air,
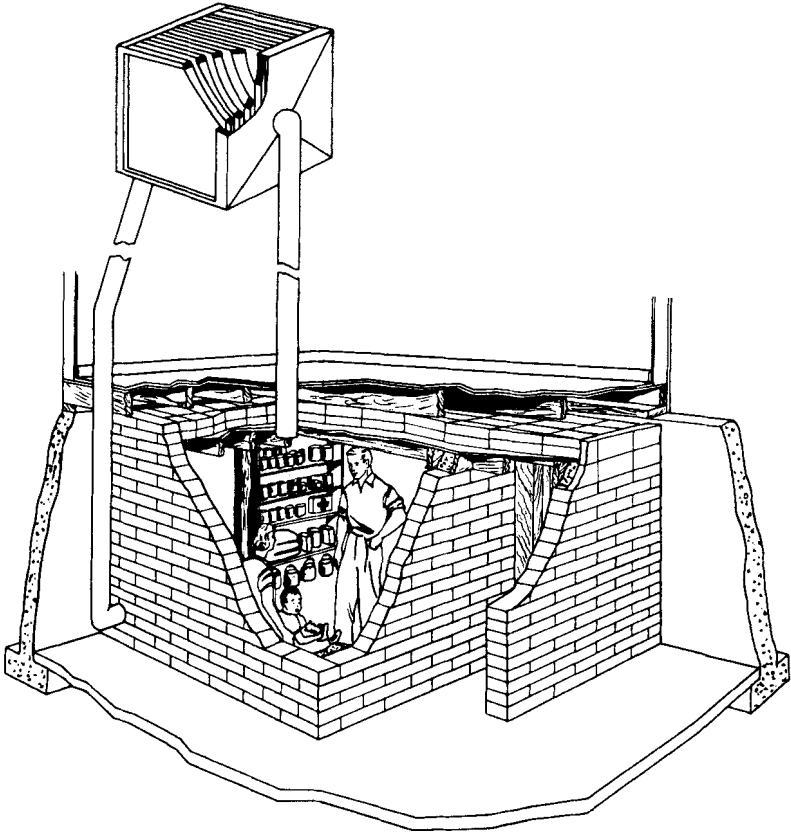
FIGURE 9.   Fallout shelter utilizing a membrane air regenerator.

which is usually the case. Were this not so, a very low-powered fan could be used to circulate the breathing air through the membrane package.

The performance of such a system was tested in an experimental apparatus containing two mice (FIGURE 10). Approximately one-third of a square yard of 1-mil silicone membrane was used in a four-ply cell, with a small bellows pump circulating interior air past the membrane. For 11 days, the animals were sustained by the membrane, the CO_2 averaging approximately 1%, and the O_2 averaging 14%.

During the twelfth day, mold began growing on feces, which increased the O_2 consumption rate to the extent that the membrane package could no longer maintain breathable air. At that point, the cell was opened; and the mice were still in good health. Certainly, better housekeeping would have eliminated this problem and theoretically allowed the system to operate indefinitely.

Oxygen Extraction from Fresh Water

As with many other polymer-liquid systems, the rate of H_2O permeation through silicone rubber is determined only by its partial pressure gradient and is

independent of whether the high-pressure side of the membrane is in contact with saturated water vapor or liquid water. Even if liquid water is pressurized, its rate of permeation is little changed. Although 1000 psi hydrostatic pressure on liquid water raises its vapor pressure about 5%, the resultant slight increase of water transport rate is small return for the cost of pressurization.

Now if the water contains a dissolved gas, its activity will be equal to its partial pressure in the gas phase with which the water is in equilibrium. Thus, a supported membrane with one side evacuated and the other supplied with a stream of air-saturated water will transmit air as well as water vapor. Therefore, at 15°C, a 1-yd^2 membrane 1-mil thick with vacuum on one side and air-saturated water on the other side could permeate the following amount of each component: 11 liters O_2/hr, 18.2 liters N_2/hr, 52 grams H_2O/hr.

In actual practice, there will be some depletion of dissolved air in the water next to the membrane, reducing the O_2 and N_2 fluxes through the membrane. In fact, the highest air rate measured was one-half that observed with the membrane exposed to ordinary air. In other words, the water at the membrane surface was 50% saturated; this unsaturated layer might be thought to have added an effective resistance equal to that for the 1-mil silicone membrane. However, this boundary layer resistance only increases the area of membrane required for a given air supply. Since the water in the ocean is fairly well saturated with dis-
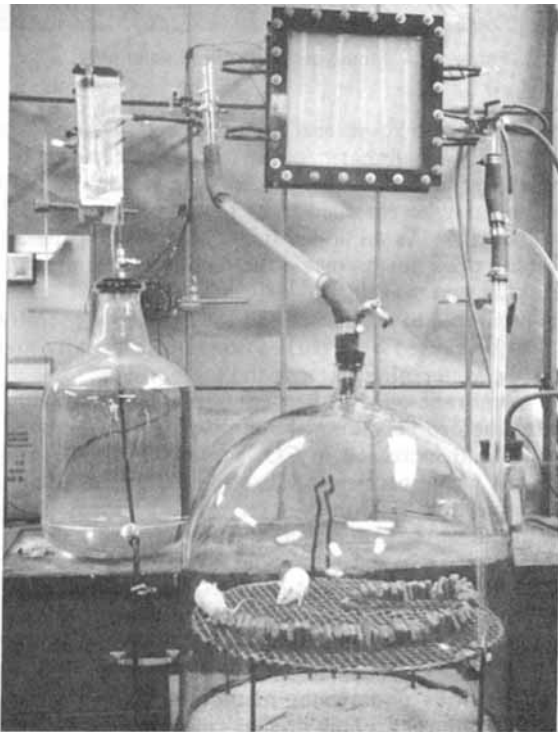

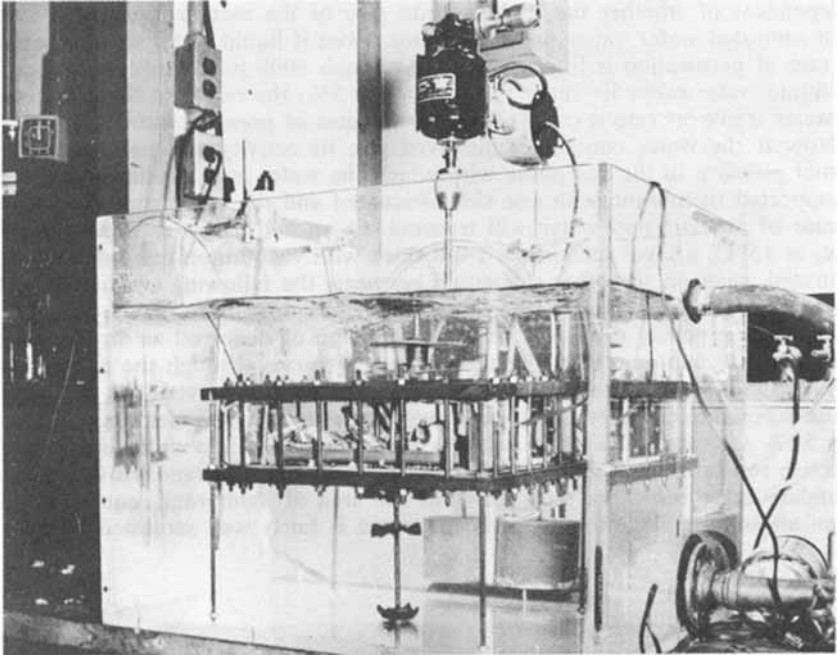FIGURE 10.   Mouse cage and air regenerator used in 11-day test.

FIGURE 11.   Mouse cage with gill in water tank.

solved air at least to a depth of several hundred meters,[14] one can consider the use of a membrane gill for submarines and underwater stations.   ,

Because of the higher solubility of O_2 than N_2 in water and the higher permeability of O_2, the gas may be enriched to as high as 35% O_2 (dry basis) as per the O_2 enricher of Part A. As an added bonus, the water permeating the membrane is salt free (salt does not permeate the membrane) and may be condensed and used for drinking and washing.

In a manner comparable to that described for the air regenerator, O_2 and CO_2 permeation can also be caused by a partial pressure or activity gradient between the air phase and the water phase across the membrane.

Therefore, if a membrane-covered box containing a man or other animal were placed under water, before very long the atmosphere in the box would be partially depleted in O_2 and increased in CO_2 content. However, this would result in O_2 dissolved in the water permeating through the membrane and entering the box, while at the same time CO_2 in the box would permeate through the membrane, dissolving in the water. As long as fresh water continued to flow over the membrane, the atmosphere in the box could be maintained in a habitable state although somewhat depleted in O_2 and slightly enriched in CO_2. Of course, the air in the box would become saturated with water vapor, but this would happen initially, and then very, very little water would be transferred through the membrane.

A demonstration of this underwater membrane system was made with the apparatus shown in FIGURE 11. This animal cage was covered top and bottom with about 200 in² of 1-mil silicone membrane. The film was backed with a

porous Dacron paper resting on a fine copper screen and supported by a punched copper plate—all to ensure that water pressure would not collapse the membrane.

Connected to the cage was a completely enclosed bellows pump to circulate the enclosed air through a Beckman O_2 meter. Four clear Plexiglas sides permitted close observation of the inhabitant—a 24-gram mouse. A large supply of food was initially included with the mouse, but drinking water was provided by means of a cold water condenser installed in the side of the box. During the extent of the experiment, moisture permeating into the cage and condensing on this cold surface provided a continuous supply of fresh water. In order to maintain air-saturated water at the membrane surface, two 4-inch-diameter stirrers operating at 100 rpm circulated water aerated with a sintered glass air bubbler.

Since the mouse consumed approximately 2.2 cc of O_2 a minute and the volume of the box was 7000 cc, the O_2 content of the box initially decreased at a rate of about 2%/hr. But within two hours the rate of decrease had tapered off substantially, and in six hours the O_2 content had become constant at 15% O_2. For three days the O_2 content remained near 15%, decreasing only towards the end of the fourth day. This decrease was due to (1) molding of food which had dropped into the mouse's drinking water and (2) some water leakage into the cage, which eventually blocked off most of the lower membrane.

A similar experiment was performed with the cell shown in FIGURE 12. This cage, one foot on a side, has approximately three ft² of membrane surface. It is held in the middle of a water-filled tank, with about one inch of clearance around the membrane. Water is pumped out of the tank and returned through
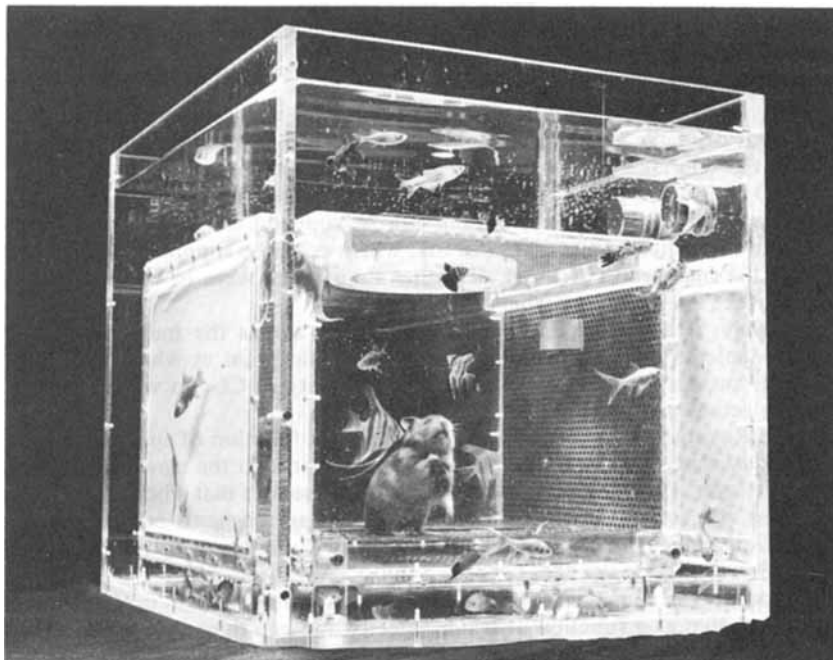

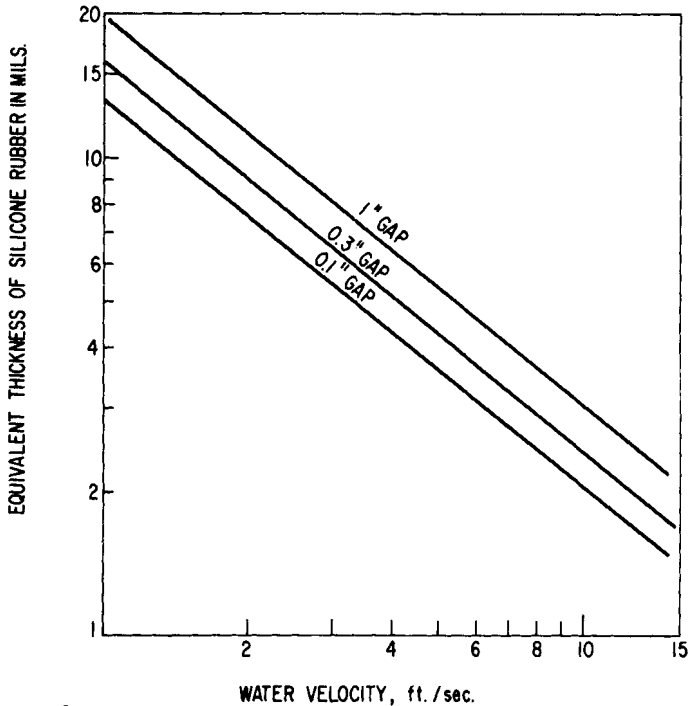FIGURE 12. Hamster in submerged cage with silicone membrane sides.

FIGURE 13.   Water boundary layer thickness for mass transfer expressed in equivalent mils thickness of silicone rubber.

a nozzle, which directs the water stream against the one side of the cage. When ten gallons of water a minute are pumped around the cage, oxygen can be supplied to the contained atmosphere at a rate of 2.5 cc/min. This is sufficient to supply O_2 for a 30-gram hamster and, at the same time, remove the CO_2 it produces. With this geometry, oxygen can be supplied to the contained atmosphere at a rate equal to one-eighth of that which could be supplied by permeation through the membrane, if fresh air rather than water were in contact with the outer surface of the membrane.

Obviously, if the water is not kept in motion across the membrane, it will become depleted in O_2 and enriched in CO_2 to the point at which the gill can no longer sustain life. Because of the high solubility of CO_2 in water, O_2 depletion will actually be limiting in this instance.

By the Reynolds analogy, one can calculate as a function of spacing and average velocity a mass transfer coefficient for gases through the slow-moving water boundary layer. If one wishes, by making use of the fact that silicone rubber has five times the oxygen permeability that water has, one can equate the mass transfer resistance of the water boundary layer to an equivalent thickness of silicone rubber.

In FIGURE 13, the boundary layer thickness in equivalent mils of silicone rubber is shown as a function of water velocity and gap thickness. For a velocity of three ft/sec in a gap width of one inch, it is seen that the boundary layer is equivalent to approximately eight mils of silicone rubber. These are approxi-

mately the conditions found in the gill shown in FIGURE 12. Actually, somewhat less water boundary layer resistance was found experimentally, probably due to the additional mixing brought about by the flow around corners and against the membrane. It is seen that, at a 10-ft/sec water flow rate, the boundary layer resistance can get fairly low.

Sea water contains approximately 6 cc of O_2 per liter. Assuming a gill can remove 5% of this oxygen, about 40 ft^3/min of water would have to pass through the gill to supply O_2 for a man at rest. Obviously this flow can be achieved either by moving the gill through the water, or by pumping water through a stationary gill.

Unfortunately, the oxygen extraction unit is much less efficient than the gill of a fish. With the oxygen extraction unit, an air phase has been interposed between water and the blood in the lungs, requiring the O_2 to permeate two membranes. Also, the man must be kept in a rigid container such as a submarine hull, for otherwise there is no way to keep his lungs from being collapsed by the water pressure.

Admittedly, to go a step further, one might consider circulating the blood through an external gill containing a silicone rubber membrane in contact with the sea water. Thus the body would be at ambient pressure, provided the lungs were filled with compressed gas or liquid.

This introduces some additional difficulties, not the least of which is the fact that man is warm-blooded. The loss of body heat to cold water would be intolerable, without a regenerative heat exchanger between the human body and the gill. It would also be important that osmotic pressures of the blood and water be in reasonable balance, as would be the case in salt water. While these are very serious problems, there is no theoretical reason to prevent building a true artificial gill, should the incentive ever warrant its development and installation.

Acknowledgments

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