Oxygen Permeation Through Teflon–PFA Tubing into Flowing Helium

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SYNOPSIS

The permeability coefficient for oxygen diffusing through a sample of Teflon–PFA tubing has been determined experimentally. The source of the diffusing oxygen was ambient air surrounding a 1.835 m length of PFA tubing. Pressurized high purity helium was directed through the center of the PFA tubing. Oxygen permeating from the low pressure ambient air source, through the PFA tubing, and into the flowing pressurized helium was observed in the effluent gases as they passed through a trace oxygen analyzer. By this means, oxygen concentrations in the effluent helium were determined as a function of varying helium flow rates, at helium gas pressures of 1.92 and 4.40 atm (absolute), within the tubing bore. All measurements were carried out at ambient temperatures of 23.5 ± 1.3°C. In addition, a theoretically related graphical method of evaluating the experimental data was employed to actually determine the oxygen permeability coefficient for this system.

INTRODUCTION

In a recent paper,[1] the permeability behavior of oxygen (in air) diffusing through a sample of Teflon–PFA tubing, into a flowing stream of pressurized nitrogen, was studied experimentally. One result of that study was a determination of the permeability coefficient[2,3] for the oxygen/Teflon–PFA system. In addition, it was noticed that the oxygen permeability coefficient of the Teflon–PFA tubing seemed to be influenced by the type of gas flowing through the bore of the tubing. Although this effect has been observed in the past,[4,5] there are no experimental studies, known to the author, which have examined this phenomenon in detail. Therefore, the present experimental study was undertaken in order to place some of this behavior on a more quantitative basis. Specifically, the PFA bore side flow of gas was changed from nitrogen to high purity helium and new oxygen permeability measurements were made. There was a significant difference between the oxygen permeability coefficient determined in this way and the oxygen permeability coefficient determined when flowing nitrogen was passed through the bore of the PFA tubing.

EXPERIMENTAL

The apparatus employed in order to facilitate this work was substantially equivalent to the equipment used during an earlier experimental study.[1] However, one obvious change involved the pure gas source fed through the bore of the Teflon–PFA tubing. In the present study, this gas source was a large cylinder (size 49) of high purity helium. Another change involved the use of a much shorter section of PFA tubing (i.e., 1.835 m) instead of the longer section of tubing used during our initial study. The shorter section of tubing was used so that easily measurable concentrations of oxygen (which diffused into the flowing helium) could be created without the need to use very high helium flow rates. This shorter section of PFA tubing had the same i.d. and o.d. (i.e., 1.588 mm and 3.175 mm) and was purchased at the same time as the PFA tubing employed earlier. As in the earlier study, air surrounding the outside of the PFA tubing also provided the source of oxygen which diffused into the high purity helium flowing through the bore of the PFA tubing. Helium flow rates, through the PFA tubing, were varied from about 0.50 to 1.33 slpm (standard liters per minute, 0.0°C and 1.0 atm). The uncertainty in these flow rates was about ±5%. In addition, the helium gas

pressure within the tubing was held constant for one series of trials at 1.92 atm and for a second series of trials at 4.40 atm. The maximum uncertainty in these gas pressures was about ±3.5%.

All oxygen concentration measurements were made, as in the past, using a Delta F Trace Oxygen Analyzer (Model FA 30111A, Delta F Corp., Woburn, MA). These oxygen concentration measurements were made on either the 0.0–10.0 ppm or 0.0–100 ppm scale ranges of this instrument. Readings on the 0.0–10.0 ppm scale could be made to the nearest 0.05 ppm level with an estimated uncertainty of about ±0.20 ppm. Readings on the 0.0–100 ppm scale could be made to the nearest 0.5 ppm level with an estimated uncertainty of about ±2.0 ppm.

The quality of the high purity helium supply was checked, using the Delta F instrument, in a separate experimental trial in which the helium was passed directly into the trace oxygen analyzer without first passing through the PFA tubing. This test indicated a residual quantity of oxygen, in the helium, at the 2.05 ± 0.20 ppm level. This oxygen concentration was subtracted from all of the oxygen permeate concentrations subsequently measured in the helium which passed through the PFA tubing. This correction was necessary in order to estimate what levels of oxygen would have been produced in the flowing helium in the event that there had been no initial oxygen impurity in the helium.

During the course of this experimental study, the average ambient temperature was about 23.5 ± 1.3°C and the average barometric pressure was 742.4 ± 2.3 mm Hg (corrected for temperature and latitude). It is believed that these temperature and barometric pressure variations were too small to cause any appreciable effect on the permeability measurements. However, it is well known that larger temperature variations can produce significant changes in gaseous permeability coefficients.[4] In any case, the average barometric pressure and volume percentage of oxygen in air (i.e., 20.9%) indicate that the partial pressure of oxygen in the air was approximately 15.5 cm Hg throughout all of the experimental trials.

RESULTS AND DISCUSSION

Some of the primary experimental conditions and results of this study are listed in Table I. It should be noted that several measurements were repeated (under practically identical conditions, but at different times) in order to determine the variability that could be expected in repeated trials. The differences in the results obtained during these trials were primarily due to the experimental errors (un-

certainties) in the flow rate measurements and the oxygen concentration measurements (both on the order of ±5%). Other errors, although present, were relatively small. As explained and noted in the past for other combinations of gases,[1,6] there is a linear relationship between the induced oxygen impurity concentration and the reciprocal of the helium gas flow rate. This relationship has been illustrated in Figure 1. In addition, this illustration also demonstrates that the oxygen permeability behavior is insensitive to the helium pressure within the permeable tubing. However, this effect could not be expected to hold if the gas pressure, either inside or outside of the tubing, was high enough to appreciably change the tubing dimensions.[7-10]

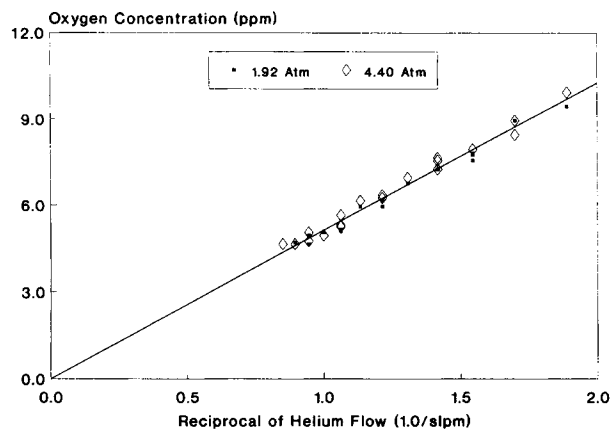**Table I   Oxygen Permeation through Teflon–PFA Tubing into Flowing Helium[a,b]**

Helium Gas Flow Rate[c] (slpm)	Oxygen Concentration in Effluent Helium (ppm)[d], Helium Pressure in Tubing Bore	
	1.92 atm	4.40 atm
0.85	—	4.65
0.89	4.70	4.65
0.94	4.65	4.75
0.94	4.95	5.05
1.00	5.05	4.95
1.06	—	5.25
1.06	5.15	5.65
1.06	5.10	5.30
1.13	5.95	6.15
1.21	—	6.35
1.21	5.95	6.25
1.21	6.15	6.35
1.31	6.75	6.95
1.42	—	7.55
1.42	—	7.65
1.42	7.25	7.25
1.54	7.80	—
1.54	7.55	—
1.54	7.75	7.95
1.70	8.95	8.95
1.70	8.95	8.45
1.89	9.45	—
1.89	9.45	9.95

[a] Oxygen partial pressure over outer surface of tubing was nearly constant at 15.5 cm Hg.

[b] Tubing length = 1.835 m, o.d. = 3.175 mm, i.d. = 1.588 mm, average temperature = 23.5 ± 1.3°C.

[c] Units are slpm (standard liters per minute, 0°C and 1 atm).

[d] These concentrations have been corrected by subtracting the initial oxygen impurity concentration in helium (i.e., 2.05 ± 0.20 ppm) from the values measured during each trial run. Therefore, the numerical uncertainty in the corrected values is ±0.40 ppm.

Figure 1 Oxygen permeation through Teflon–PFA tubing into flowing helium.

Another effect is implied by the plot in Figure 1, i.e., in the limit of infinitely high helium flow rates, the induced oxygen impurity concentration must approach zero. In other words, the Y intercept of the best fit line through the data points in Figure 1 must be zero. This fact provides a means of checking the zero point accuracy of any analytical instrument which is sensitive to specific permeate impurities which can be measured using the technique described herein.

In addition to some of the points mentioned above, it should also be noted that the linear behavior exhibited in Figure 1 will not always hold. For example, one of the conditions which helps to promote this linearity is that the internal partial pressure of the dopant gas (in this case, oxygen) must be very small (throughout the length of the tubing) relative to its constant external partial pressure. If this condition is satisfied and if all other possible variables are held constant, the driving "force" tending to promote the inward diffusion of oxygen (namely, the concentration gradient) will be relatively constant throughout the length of the permeable tubing. If, however, the permeable tubing is relatively long, or if the "clean" gas flow rate through the bore of the tubing is too low, the impurity concentration will build up in the flowing "clean" gas and progressively inhibit the downstream inward diffusion of oxygen. In other words, the concentration gradient will decrease axially and the net result will produce concavity (toward the X-axis) in an impurity concentration versus reciprocal flow rate plot. This condition was studied experimentally by making an additional series of measurements using very low flow rates of helium. The results of these measurements have been plotted in

Figure 2. One of the main things to note from this plot is that deviations from the initial linearity, at helium flow rates greater than ca. 0.5 slpm, are pronounced. This effect does not appear to be related to a transition from turbulent to laminar flow. In fact, the Reynolds number for a helium flow rate of 0.5 slpm (in the PFA tubing used during this study) is slightly less than 60. This Reynolds number is much smaller than the Reynolds numbers of 2000–3000 which normally characterize the transition between laminar and turbulent flow.[11] In any case, as long as one uses only the linear portion of the curve (i.e., the region of the curve in which the helium flows are greater than 0.5 slpm), the methods described in Ref. 1 will produce a reasonably accurate value for the oxygen/PFA permeability coefficient when helium is passed through the bore of the PFA tubing. This permeability coefficient will also be an explicit predictor of oxygen permeation behavior for all other helium flows within the straight line plot region.

The equation of the straight line drawn through the experimental data points in Figure 1 was determined using a least squares computer curve fit. However, the X, Y coordinates of this line at its origin (i.e., 0,0) were not allowed to vary during the curve fitting routine.[12] Using this technique, the equation of the straight line is

$$Y = 5.14X$$

where Y is the oxygen permeate concentration (in ppm) and X is the reciprocal of the helium gas flow rate (in units of 1/slpm). The slope of this line (i.e., 5.14 ppm slpm or 5.14×10^{-6} slpm) and the methods described earlier[1] were used to calculate the permeability coefficient for oxygen diffusing through
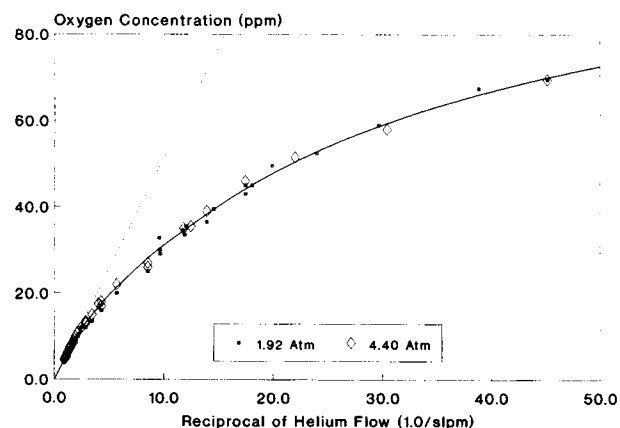
Figure 2 Oxygen permeation through PFA tubing: nonlinear curve region.

Table II Comparison of Teflon–PFA Permeability Coefficients[a]

Permeating Gas	"Clean" Gas	Permeability Coefficient[b] $\times 10^8$ [cm^3 (stp) mm]/[cm^2 s cm Hg]	Reference
Oxygen	Nitrogen	1.03	1
Oxygen	Helium	3.06	This study
Carbon dioxide	Nitrogen	1.53[c]	6

[a] All values were determined at ambient temperatures in the range of 20–25°C.

[b] The uncertainty in the values listed below is approximately ±10%.

[c] The originally published value for this permeability coefficient[6] was expressed with incorrect units, i.e., the pressure unit torr was used in place of the intended unit cm Hg.

the Teflon–PFA membrane and into the flowing helium gas. The oxygen permeability coefficient, determined in this way, is

$$3.06 \times 10^{-8} \, [\text{cm}^3 \, (\text{stp}) \, \text{mm}]/[\text{cm}^2 \, \text{s} \, \text{cm Hg}]$$

The units employed above have been used so that this value of the permeability coefficient could be easily compared with other tabulated permeability coefficients.[1,4,6,13–17] A few of these permeability coefficients are listed in Table II. It may be seen that there is a significant difference between the two listed oxygen permeability coefficients for the oxygen/Teflon–PFA system. This difference depends solely (for all practical purposes) upon the type of gas passing through the bore of the PFA tubing. Specifically, the oxygen permeability coefficient of the PFA tubing, when helium is passed through the tubing bore, is about three times greater than the oxygen permeability coefficient which results when nitrogen is passed through the same type of tubing. This is an extremely interesting fact which has several practical implications with regard to the use of permeation as a means of doping selected gas (or gas mixture) streams. There must also be other consequences of this behavior when permeation techniques are used to separate selected gas mixtures.

CONCLUSION

A primary result of this study is an experimentally determined value of the permeability coefficient for the diffusion of oxygen through a membrane made of Teflon–PFA tubing and into a flowing stream of pressurized helium. It has also been demonstrated that the magnitude of the oxygen permeability coefficient depends upon the type of initially "clean" gas flowing through the bore of the PFA tubing. This effect is significant. At present, there does not seem to be any quantitative explanation for this phenomenon. In addition, it is believed that future experimental studies of this behavior will be essential in order to develop a better understanding of the process of gaseous permeation.

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