Oxygen Permeation through Teflon–PFA Tubing into Flowing Argon

INTRODUCTION

In two recent articles,[1,2] the permeability behavior of oxygen, diffusing through a sample of Teflon–PFA tubing and into a flowing stream of an inert gas (pressurized nitrogen or helium), was studied experimentally. These studies permitted a determination of permeability coefficients[3,4] for the oxygen/Teflon–PFA system. However, it was noticed that these permeability coefficients were influenced significantly by the type of gas flowing through the bore of the tubing. Although this effect has been observed in the past,[5,6] there are no experimental studies (other than our own) known to the author that have examined this phenomenon in detail. Therefore, the present experimental study was undertaken in order to place more of this behavior on a quantitative basis. Specifically, the PFA bore side flow of gas was changed to high purity argon and new oxygen permeability measurements were made.

EXPERIMENTAL

The apparatus employed in order to facilitate this work was substantially equivalent to the equipment described earlier.[1] However, one obvious change involved the pure gas fed through the bore of the Teflon–PFA tubing. In the present study, this gas source was obtained from a large (150 L) Dewar of high purity liquid argon. The long section of PFA tubing (15.754 m), employed during this study, 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 our earlier studies, the air surrounding the outside of the PFA tubing provided the source of oxygen, which diffused into the high purity argon flowing through the bore of the PFA tubing. Argon flow rates, through the PFA tubing, were varied from about 0.50 to 2.0 slpm (standard liters per minute: 0.0°C, 1.0 atm). The uncertainty in these flow rates was about ±5%. In addition, the argon gas pressure within the tubing was held constant for one series of trials at 2.19 atm and for a second series of trials at 4.40 atm. The maximum uncertainty in these gas pressures was about ±0.8%.

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

to 10.0 ppm or 0.0 to 100 ppm scale ranges of the Delta F Analyzer. Readings on the 0.0 to 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 to 100 ppm scale could be made to the nearest 0.5 ppm level, with an estimated uncertainty of about ± 2.0 ppm.

During the course of this experimental study, the ambient temperature was about 22.6 ± 1.6°C, the barometric pressure was 746.3 ± 3.2 mmHg (corrected for temperature and latitude), and the relative humidity of the laboratory air was about 21 ± 3%. It is believed that the temperature, barometric pressure, and relative humidity 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.[5] In any case, using the barometric pressure listed above, and the nominal volume percentage of oxygen in dry air (i.e., 20.95%), the partial pressure of oxygen in the air was taken to equal 155.4 ± 0.8 mmHg (corrected for moisture content in the air) throughout all of the experimental trials.

RESULTS AND DISCUSSION

Some of the primary experimental conditions and results of this study may be seen in Table I. It may also be seen 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 some of these trials were primarily due to the experimental errors (uncertainties) in the flow rate measurements and the oxygen concentration measurements. Other errors, although present, were relatively small. As explained and noted in the past for other combinations of gases,[1,2,7] there is a linear relationship between the induced permeate impurity concentration and the reciprocal of the bore side gas flow rate. This relationship has been illustrated in Figure 1. Figure 1 also demonstrates that the oxygen permeability behavior is insensitive to the argon 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 change appreciably the tubing dimensions.[8-11]

The equation of the least squares, curve fitted,[12] straight line (correlation coefficient = 0.9987) drawn through the experimental data points in Figure 1 is:

$$Y = (13.46 \pm 0.54)X + 1.02$$

Table I   Oxygen Permeation through Teflon–PFA Tubing into Flowing Argon.[a,b]
Oxygen Concentration in Effluent Argon (ppm)

Reciprocal of Argon Gas Flowrate[c] $(slpm)^{-1}$	Argon Pressure in Tubing Bore	
	2.19 atm	4.40 atm
0.54	7.65	8.25
0.54	8.10	8.40
0.54	7.60	8.35
0.54	—	8.35
0.57	—	8.80
0.58	8.80	8.90
0.59	8.80	—
0.60	—	9.60
0.62	—	9.60
0.63	9.85	—
0.65	9.35	9.90
0.66	9.32	—
0.68	—	10.5
0.70	11.0	10.9
0.70	10.2	—
0.72	10.5	11.0
0.74	11.0	11.0
0.74	11.5	10.5
0.80	12.0	11.5
0.80	—	12.5
0.82	11.5	12.0
0.82	11.5	12.5
0.85	13.0	12.0
0.94	13.0	—
0.94	14.0	—
0.97	14.0	14.5
0.97	14.0	15.0
1.05	—	15.0
1.09	16.5	—
1.09	15.0	—
1.13	15.0	15.5
1.13	—	16.0
1.13	—	16.5
1.24	17.5	—
1.30	18.5	18.5
1.30	18.5	—
1.36	18.5	—
1.43	—	20.5
1.43	—	21.0
1.51	—	22.5
1.60	—	23.0
1.81	24.5	—

[a] Oxygen partial pressure over outer surface of tubing was nearly constant at 155.4 ± 0.8 mm Hg.
[b] Tubing length, o.d. and i.d.: 15.754 m, 3.175 mm, 1.588 mm. Average temperature: 22.6 ± 1.6°C.
[c] Units are $(slpm)^{-1}$, where slpm stands for standard liters per minute (i.e., 0°C and 1 atm).

where Y is the oxygen permeate concentration in ppm units, 13.46 ± 0.54 is the line's slope (± one standard deviation[13]) in units of ppm × slpm, X is the reciprocal of the argon gas flow rate in units of $(slpm)^{-1}$, and 1.02 is the Y-intercept of the straight line. This nonzero intercept is due to the combined effect of a small residual oxygen impurity concentration in the argon gas source and a slight error in the zero point setting in the trace oxygen analyzer. If there were absolutely no oxygen impurities in the argon gas and no zero point error in the trace oxygen analyzer, the intercept value of this line would have been exactly zero because at infinitely high argon flow rates (i.e., at $X = 0.0$) the amount of oxygen diffusing into the argon would have been negligible. A knowledge of these effects, which do not seem to be generally known, can be extremely useful because they permit one to obtain relatively accurate corrections in this type of experimental data without an exact measurement of initial impurity concentrations in the test gas, or the need to make a precise adjustment in the zero point setting of the trace gas analyzer. In any case, this nonzero intercept value has absolutely no influence on the oxygen/Teflon–PFA permeability coefficient determined below, because a correction for this effect will not change the slope of the experimentally determined straight line and it is the slope alone that must be used to determine the permeability coefficient for the Teflon–PFA membrane.[1] Therefore, using the method described in detail earlier,[1] and the slope of the straight line indicated in Figure 1 (i.e., 13.46 ppm × slpm or 13.46×10^{-6} slpm), the permeability coefficient for oxygen diffusing through the Teflon–PFA membrane and into the flowing argon gas was calculated. The oxygen permeability coefficient, determined in this way, is:

$$(0.93 \pm 0.04) \times 10^{-8}$$

$$[cm^3(stp) \times mm]/[cm^2 \times sec \times cm\ Hg].$$

The uncertainty in this permeability coefficient (i.e., $\pm\ 0.04 \times 10^{-8}\ [cm^3(stp) \times mm]/[cm^2 \times sec \times cm\ Hg]$) was determined directly from the standard deviation in the slope of the straight line in Figure 1, because all other experimental errors were small compared to the error in the slope of this line.

The units employed above have been used so that this value of the permeability coefficient could be easily compared with other tabulated permeability coefficients.[1,2,5,7,14–18] A few of these permeability coefficients have been listed in Table II. It may be seen that there is a significant difference between the oxygen permeability coefficients determined when either nitrogen or argon was passed through the tubing bore instead of helium. This difference seems to depend 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 that results when argon or nitrogen is passed through the same type of tubing.
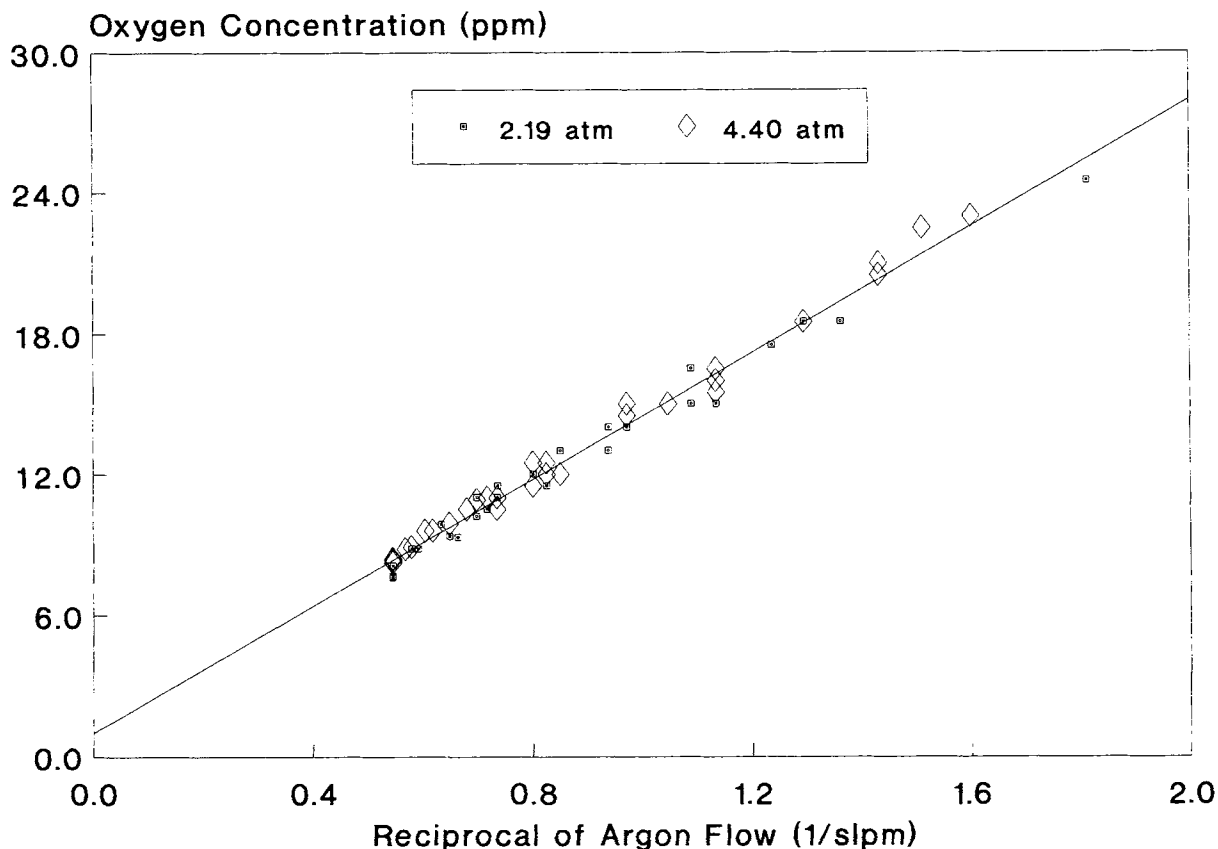
Figure 1 Oxygen permeation through teflon–PFA tubing into flowing argon.

This is an 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 are also other consequences of this behavior when permeation techniques are used to separate selected gas mixtures.

CONCLUSIONS

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 argon. It is also clear that the magnitude of the oxygen permeability coefficient depends upon the type of initially "clean" gas flowing through the bore of the PFA tubing and that this effect can be significant. At present, there still does not seem to be any quantitative explanation for this phenomenon. However, it is hoped that ongoing experimental studies, in our laboratory, will lead to a better understanding of the physical and/or chemical process that is responsible for this behavior. We hope to report on the results of these ongoing studies at a later date.

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

"Clean" Gas	Permeability Coef.[b] $\times 10^8$ $[cm^3(stp) \times mm]/[cm^2 \times sec \times cm\ Hg]$	Reference
Nitrogen	1.03	1
Helium	3.06	2
Argon	0.93	This Study

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

[b] An uncertainty of ±5% in the values listed below represents approximately ± one standard deviation.

References

1. F. W. Giacobbe, *J. Appl. Polym. Sci.*, **39**, 1121–1132 (1990).
2. F. W. Giacobbe, *J. Appl. Polym. Sci.*, **42**, 2361–2364 (1991).
3. R. E. Treybal, *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York, 1980, p. 94.
4. F. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1979, p. 45.
5. S. A. Stern, *Industrial Processing with Membranes*, R. E. Lacev and S. Loeb, Eds., Wiley–Interscience, New York, 1972, Chap. XIII, pp. 279–339.
6. C. R. Rogers, *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Lobes, and A. Weissberger, Eds., Wiley–Interscience, New York, 1965, Vol. II, Chap. 6, pp. 510–627.
7. F. W. Giacobbe, *Mater. Letters*, **9**, 142–146 (1990).
8. J. M. Thorman and S. T. Hwang, *Chem. Eng. Sci.*, **33**, 15–20 (1978).
9. S. A. Stern, F. J. Onorato, and C. Libove, *AIChE J.*, **23**, 567–578 (1977).
10. C. T. Blaisdell and K. Kammermeyer, *AIChE J.*, **18**, 1015–1019 (1972).
11. S. A. Stern, S. M. Fang, and H. L. Frisch, *J. Poly. Sci.*, **A-2**, 201–219 (1972).
12. EnPlot, Version 2.0, ASM International, Materials Park, OH (1989).
13. The standard deviation in the slope was determined by using all pairs of X–Y data (as well as the intercept value of 1.02 ppm) in Table I in order to calculate 59 separate and independent slope values. Then, elementary statistical methods were used to calculate the standard deviation in the mean slope value.
14. K. H. Lee and S. T. Hwang, *J. Colloid and Inter. Sci.*, **110**, 544–555 (1986).
15. P. H. Perry and C. H. Chilton, Eds., *Chemical Engineer's Handbook*, 5th ed., McGraw-Hill, New York, 1973, pp. 17, 34–37.
16. C. E. Rogers and S. Sternberg, *J. Macromol. Sci.-Phys.*, **B5**(1), 189–206 (1971).
17. K. Kammermeyer, *Ind. Eng. Chem.*, **49**, 1685–1686 (1957).
18. D. F. Othmer and G. J. Frohlich, *Ind. Eng. Chem.*, **47**, 1034–1040 (1955).

F. W. Giacobbe

Chicago Research Center
American Air Liquide, Inc.
Countryside, Illinois 60525