Oxygen Permeability of Teflon–PFA Tubing

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Synopsis

The permeability coefficient for oxygen diffusing through a sample of Teflon–PFA tubing was determined experimentally. The source of the diffusing oxygen was ambient temperature air surrounding a coiled length of the PFA tubing. High pressure nitrogen 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 high pressure nitrogen was observed in the effluent gases as they passed through a trace oxygen analyzer. By this means, oxygen concentrations in the effluent nitrogen were determined as a function of varying nitrogen flow rates, at nitrogen gas pressures of 4.4 and 7.8 atm (absolute), within the tubing bore. All measurements were also carried out at ambient temperatures of 21 ± 1°C. In addition, a theoretically related graphical method of evaluating the experimental data was developed and subsequently employed to actually determine the oxygen permeability coefficient for this system.

INTRODUCTION

A nitrogen-based atmosphere, containing a relatively low concentration of oxygen, was needed during a recent experimental study in our laboratory. The requirements associated with that study involved the use of low flows of nitrogen, doped with oxygen, for very long periods of time. Some flexibility in varying the oxygen impurity concentration was also desired. Initially, it was thought that a series of precalibrated high pressure nitrogen cylinders containing the desired levels of oxygen impurities could be used. However, this solution was rejected due to uncertainties in our initial oxygen concentration requirements. Another potential solution which was considered involved the continuous dilution of either high pressure air or the gas from a high pressure nitrogen cylinder doped with very high levels of an oxygen impurity. This solution was also rejected due to the experimental problems and complications related to the fabrication of an accurate and reliable dilution system. As another possible solution to this problem, the idea of using a semipermeable plastic or polymeric membrane was also considered. The use of this kind of system seemed to offer much flexibility as well as a low cost alternative solution to our needs. In any case, the type of membrane which could have been useful in our application and the exact operating parameters which would have to be employed were all unknown.

A study of some of the commercially available literature related to permeation devices[1,2] as well as a number of general and more specific references related to the permeation of various gases and gas mixtures through membranes[3-10] did not clarify this problem. In addition to some of the papers referred to above, other experimental studies involving the gaseous permeability of various polymeric membranes[11-25] employed techniques or materials

which we had hoped to avoid or which would not be practical in our intended end use application. In particular, the most advantageous system for use in our application would be operable with ambient temperature air as the external source of permeating oxygen while an internal flow of pure (or relatively pure) nitrogen passed through the center of a hollow length of gas permeable tubing. Under steady state conditions of temperature, internal gas flow, and pressure it was hoped that this type of system could be used to produce predetermined, reasonably constant, and very low concentration levels of oxygen in the internal flow of nitrogen gas. The oxygen-doped nitrogen could then subsequently be used in another application. Although a large number of related experimental papers (noted previously) and many excellent modeling studies exist in the literature (e.g., Refs. 26–39), no experimental study or mathematical analysis directly related to this experimental technique could be found. This is probably a direct result of the fact that, in most cases studied previously, experimental and theoretical work has emphasized the separation and purification of gas mixtures rather than the inverse process which has been described above. Therefore, in order to evaluate the feasibility of this technique, an experimental study was initiated and carried out in our laboratory. Some of the results obtained during this study were of interest to us. It was thought that these results and this technique of producing oxygen-doped inert gas streams would also be of interest to many other researchers working within a wide range of other experimental areas.

In addition, during the course of this work, a unique graphical method of determining gaseous permeability coefficients may have been developed. It is difficult to be absolutely certain of this but there does not seem to be any other publication which describes this experimental technique. Therefore, due to its use herein and potential use in other applications, this method has been described in detail.

EXPERIMENTAL

In order to evaluate the feasibility of the approach outlined above, two types of Teflon (registered trade mark of the E. I. Du Pont de Nemours Co.) tubing were originally selected for initial testing. These materials have trade names of Teflon–FEP (fluorinated ethylene polypropylene) and Teflon–PFA (perfluoroalkoyl) and are readily available through several laboratory supply houses (e.g., Cole-Palmer Inst. Co.). Although some gases related permeability data on tubing made of the FEP is available,[6,8] no such data for the PFA tubing could be found. In any case, the tubing purchased for the initial testing had dimensions of 3.18 mm o.d. × 1.59 mm i.d. × 0.79 mm wall × 7.62 m (1/8 in. o.d. × 1/16 in. i.d. × 1/32 in. wall × 25 ft). This tubing was cut into several smaller sections and the ends of the shortened sections were fitted with stainless steel swagelok type fittings. All of these relatively short sections of tubing were less than 2 m in length.

A stream of purified nitrogen was fed through each of these tubes. The outlet gas stream was fed through a flow meter (±5%) and then through a Delta F trace oxygen analyzer (Model No. FA 30111A, Delta F Corp., Woburn, MA) having three separate scale ranges (i.e., 0–1.00, 0–10.0, and 0–100 ppm) and an accuracy of about ±2% of the operative full scale reading. A schematic

1) 150 l Nitrogen Dewar
2) Stainless Steel Tubing
3) Inert Gas Purifier (Optional)
4) Pressure Regulator
5) Pressure Gage
6) Stainless Steel Bypass Line
7) Three-Way Valve (2)
8) Flow Meter
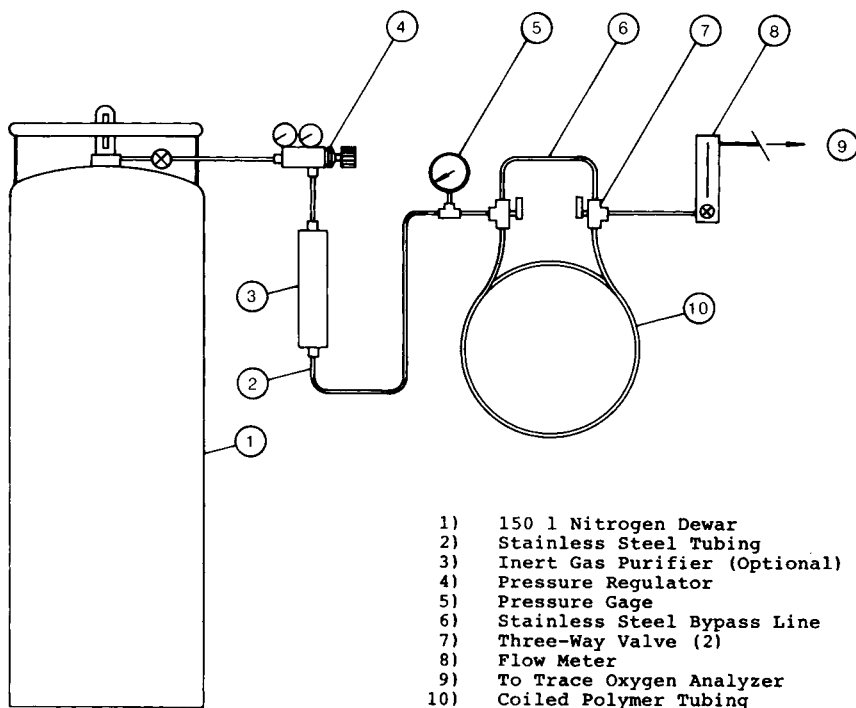9) To Trace Oxygen Analyzer
10) Coiled Polymer Tubing

Fig. 1.   Schematic of apparatus and equipment used during oxygen/teflon–PFA permeability study.

illustration showing some of this apparatus and equipment may be seen in Figure 1. During each experimental trial, gas flow rates and pressures, within the gas permeable tubing, were maintained at relatively constant levels. However, slight variations in these parameters as well as variations in the atmospheric pressure and room temperature tended to produce some scattering in the oxygen permeability results. The actual ambient temperature and variations therein were about 21 ± 1°C throughout all experimental trials. The average atmospheric pressure during all experimental trials was approximately 74.5 cm Hg. Since the volume percentage of oxygen in air is about 20.9%, oxygen partial pressures were approximately 15.6 cm Hg.

During the entire course of this work, all gas flow rates were measured using flow meters originally calibrated for air at 21°C and 1.0 atm. However, in this paper, all experimental gas flow rates have been appropriately converted into equivalent flow rates at STP (0°C and 1.0 atm) and have been expressed with the units slpm (standard liters per minute).

The quality of the purified nitrogen supply was checked periodically by bypassing the gas permeable tube and allowing this gas to directly enter into the trace oxygen analyzer. This procedure indicated that trace levels of oxygen were always less than 0.02 ppm in the purified nitrogen. An analog output signal from the trace oxygen analyzer was also continuously monitored on a chart recorder for several hours before oxygen concentration levels were recorded in the effluent nitrogen gas leaving the permeable tubing. Several different tubing lengths, gas flow rates, and internal tubing pressures were

employed during the course of this experimental effort for both the FEP and PFA tubing.

As a result of the initial studies indicated above, it was determined that the PFA tubing was significantly more permeable to oxygen than the FEP tubing. However, even with the PFA tubing, oxygen concentrations in the effluent nitrogen did not exceed 5.0 ppm. It was also clear that overall tubing length was an important factor which could easily be manipulated in order to increase the concentration of oxygen in the effluent from the permeable tubing. Since oxygen levels higher than 5.0 ppm were desired in the gases to be doped using this technique, a new series of experiments employing much longer sections of only the PFA tubing were carried out. These studies were performed using a single 7.62 m (25 ft) section of PFA tubing and two separate 7.62 m sections of PFA tubing connected in series to make an equivalent 15.24 m (50 ft) section of tubing. The other tubing dimensions (i.e., i.d. and o.d.) were equivalent to those employed during the initial studies.

In addition, as in the preliminary studies described above, the analog output signal from the Delta F trace oxygen analyzer was monitored continuously for several hours before oxygen concentrations were recorded in the effluent nitrogen. In a few cases, oxygen concentrations due to permeation through the PFA tubing were also monitored for 24–48 h. Typically, there were no significant differences in the oxygen permeate concentrations due to these extended trial run times. These procedures and the extended trial run time tests were carried out in order to insure that all results could be attributed to steady state diffusion and permeation behavior.

Some other changes were also employed during this series of tests. For example, the nitrogen gas was not prepurified prior to its introduction into those longer sections of tubing. Since higher levels of oxygen were desired in the product gas, removal of trace levels of oxygen from the nitrogen was unnecessary. In any case, residual levels of oxygen in the nitrogen were measured prior to the start of these experiments. The oxygen level was initially measured at 1.8 ± 0.2 ppm. The source of this nitrogen was a 150 L (40 gal) liquid nitrogen dewar. This vessel had to be refilled once during the course of this second study. A remeasurement of the residual oxygen level in the second batch of nitrogen indicated an oxygen concentration of 1.5 ± 0.2 ppm. In order to compensate for these initial conditions and thus improve upon the accuracy of subsequently determined oxygen permeation coefficients, the residual oxygen concentrations in the nitrogen source gas were subtracted from the oxygen concentrations measured in the effluent nitrogen at end of each permeation trial run.

RESULTS AND DISCUSSION

Experimental conditions and results related to the series of measurements made using the 7.62 and 15.24 m lengths of the PFA tubing have been summarized in Table I. From this data, it is evident that the outlet oxygen concentration, in the effluent nitrogen, is proportional to tubing length when all other variables are constant. It is even more interesting and probably surprising to see that outlet oxygen concentrations are apparently independent of the flowing nitrogen gas pressure within the PFA tubing. The consis-

TABLE I
Oxygen Permeation through 7.62 and 15.24 m Lengths of PFA Tubing into Flowing Nitrogen

	Oxygen concentration in effluent nitrogen (ppm)		Corrected oxygen concentration in effluent nitrogen (ppm)	
	Internal nitrogen gas pressure			
Nitrogen gas flow(slpm)	4.40 atm (50 psig)	7.80 atm (100 psig)	4.40 atm (50 psig)	7.80 atm (100 psig)
Tubing length = 7.62 m (25.0 ft)				
0.53	15.5	15.0	13.7	13.2
0.67[a]	12.0	12.5	10.5	11.0
0.98	9.6	9.7	7.8	7.9
1.34[a]	6.5	6.6	5.0	5.1
2.14	5.3	5.2	3.5	3.4
Tubing length = 15.24 m (50.0 ft)				
0.53	27.5	28.0	27.5	26.2
0.67[a]	22.0	22.5	20.5	21.0
0.98	17.0	16.9	15.2	15.1
1.34[a]	12.0	12.0	10.5	10.5
2.14	8.9	9.0	7.1	7.2

[a]Residual oxygen concentration in the inlet nitrogen employed during collection of this data was 1.5 ppm; for the remaining data it was 1.8 ppm.

tency of this behavior indicated that this phenomenon could probably be explained theoretically. Therefore, a detailed analysis of our system (see Appendix A) was undertaken. This effort produced the following result:

$$[O_2] = [2\pi KLP_{ex}RT]/[F_{stp}P_0 \cdot \ln(b/a)] \tag{1}$$

where $[O_2]$ is the mole fraction of oxygen measured in the nitrogen leaving the end of the permeable tubing. The other variables indicated in eq. (1) have been defined in the notation section of this paper.

A careful inspection of eq. (1) indicates that oxygen permeate concentrations are in fact independent of nitrogen gas pressure, within the permeable tubing, because no internal nitrogen gas pressure terms appear either explicitly or implicitly in this expression. Another point which should be made is that the permeability constant K is a function of several variables. In the present system, some of these variables are related to the specific gas (or gases), initially present on either side of the permeable membrane as well as their relative concentrations or partial pressures. Other important variables are related to the physical and chemical properties of the membrane itself and the operating temperature of the entire system. However, if all variables, except tubing length L and flow F (in the tubing bore), are held constant, the effluent permeate concentration (in this case, the oxygen concentration) should be directly proportional to the permeable tubing length and inversely proportional to the gas flow rate. This conclusion is directly related to eq. (1). In addition, for each length of permeable tubing tested during this study, a plot of effluent oxygen concentration versus reciprocal flow should produce a
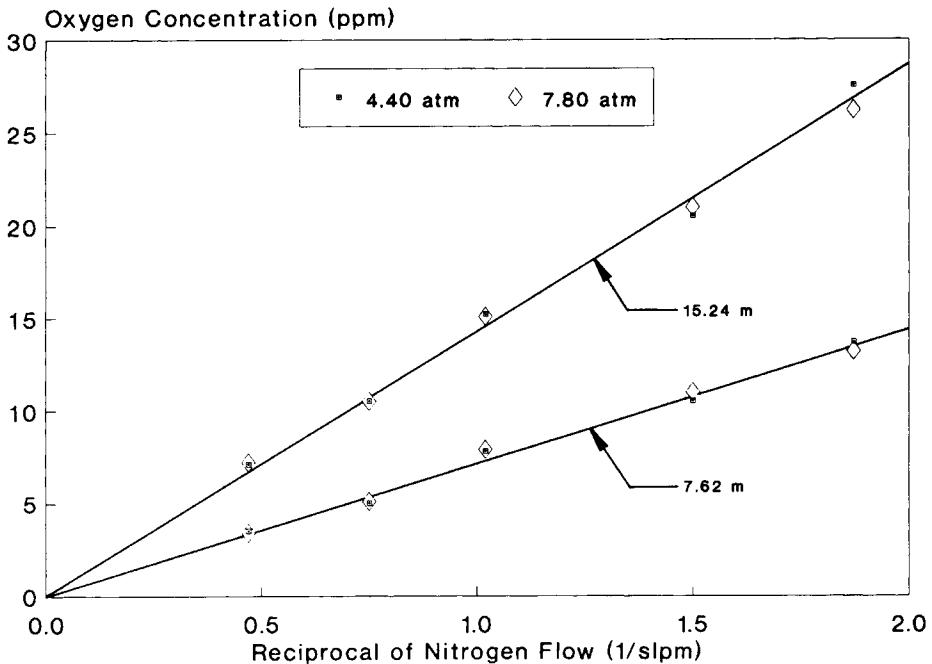
Oxygen Concentration (ppm)

Fig. 2.   Oxygen permeation through PFA tubing.

straight line with a y intercept of zero and a slope M, where

$$M = [2\pi KLP_{ex}RT]/[P_0 \cdot \ln(b/a)] \qquad (2)$$

In order to test this assumption, the data in Table I were plotted (see Fig. 2), as indicated above. Although there is some scatter in the experimental data, straight lines are clearly evident. It is also obvious that internal pressure variations, in the ranges studied herein, exhibited the predicted result (i.e., no effect). In addition, when the tubing length was doubled, the slope of the oxygen concentration versus reciprocal flow line also doubled. This effect is additionally in agreement with eq. (2) above. A simplified explanation of this behavior is that a small cylinder of gas moves through the tubing bore at a speed which is inversely proportional to pressure if the outlet flow is held constant. But the total quantity of permeate which accumulates in this small cylinder of gas is directly proportional to the time it takes for the small cylinder to pass through the tubing bore. Therefore, an identical but slower moving high pressure cylinder of gas accumulates more permeate than a faster moving low pressure cylinder of gas. However, the net effect is that the ratio of permeate volume (at STP) to carrier gas volume (also measured at STP) is the same for any fixed period of time.

It should also be understood that eq. (1) and the accuracy of any conclusions drawn from it are highly dependent upon several underlying assumptions. Namely, the internal partial pressure of the dopant gas (in this case oxygen) must always be very small relative to its constant external partial pressure. The internal and originally "clean" gas (in this case nitrogen) must

behave as an ideal or nearly ideal gas. Losses due to counterdiffusion of the clean gas should be negligible. Axial pressure drops due to flow resistances within the tubing (which can be calculated using the Poiseuille equation) can be neglected, and all tubing dimensions, as well as the permeability coefficient K, should not be seriously affected by changes in the internal or external gas pressure.

The rigidity of the PFA tubing used during this study was actually tested by measuring the o.d. of the tubing with no differential pressure applied between the i.d and o.d., and with a differential pressure of 6.8 atm between the i.d and o.d. of the tubing (the high pressure was applied in the bore of the tubing). Measurements of the tubing o.d., made to the nearest 0.025 mm, indicated no significant differences between the pressurized and unpressurized condition. For more detailed accounts of the effect of tubing elasticity and pressure upon gas permeability, the reader may wish to refer to other experimental studies (e.g., Refs. 40–43).

Finally, it is tacitly assumed that all experimental measurements are made under identical or nearly identical temperature conditions, the permeable tubing is not inordinately long, and gas flow within the tubing is not extremely low. Under either of the last two conditions, the internal partial pressure of the diffusing gas cannot be neglected with respect to its constant external pressure. In fact, in the limit, these conditions will lead to an oxygen partial pressure inside the permeable tubing equal to the external oxygen partial pressure.

Another important point with regard to eq. (2) is that this expression can be used to determine permeability coefficients for any gas diffusing through any suitable length of permeable tubing employed under the conditions described herein. All of the variables in eq. (2) (except for the permeability coefficient K) are either well-known constants or easily measurable, and the slopes of the lines plotted as in Figure 2 can be readily calculated. Therefore, values of K can be determined without difficulty. This procedure has been carried out and two independent values of the permeability coefficient, for oxygen diffusing through PFA tubing into nitrogen, have been determined. The estimated value for each slope was 7.19×10^{-6} slpm (for the 7.62 m length of tubing) and 14.35×10^{-6} slpm (for the 15.24 m length of tubing). Using these slope values in eq. (2) produced permeability coefficients of

$$1.032 \times 10^{-8} \text{ and } 1.030 \times 10^{-8} \left[cm^3(stp) \text{ mm} \right] / \left[cm^2 \text{ s cm Hg} \right]$$

or an average value of about

$$1.03 \times 10^{-8} \left[cm^3(stp) \text{ mm} \right] / \left[cm^2 \text{ s cm Hg} \right]$$

The permeability coefficient units employed above were specifically chosen so that the values calculated herein could be easily compared with other tabulated permeability coefficients.[6,8,44–46] This comparison indicated that the oxygen permeability of the PFA tubing, measured during this study, was approximately twice as great as the oxygen permeability of membranes fabricated from Teflon–FEP.[6,8] But, the oxygen permeability of natural and

several synthetic rubber membranes ranged between 2 and 60 times greater than the oxygen permeability of the PFA tubing.[6,8,46] However, natural and synthetic rubber membranes would probably not have been a good choice in our desired end use application for the PFA tubing due to their elasticity.[40–42]

Another advantage of the PFA tubing is its chemical stability. In addition, the low permeability of the PFA tubing (relative to some synthetic rubbers) requires that relatively long sections of tubing be used to produce concentrations of oxygen in nitrogen approaching 30 ppm. Therefore, the ability to precisely control oxygen dopant concentrations by varying the PFA tubing length, at fixed nitrogen flow rates, is significantly enhanced.

Instead of employing the graphical technique, outlined above, permeability coefficients may also be determined directly from eq. (1). In this case, eq. (1) is solved for K and all of the variables required to make the calculation must be measured only once. This technique, however, is not recommended because, generally, it will not produce results as accurate as those which can be obtained when the graphical technique, described above, is employed.

Other related applications of some of the techniques outlined herein are also possible. For example, permeation coefficients of multielement identical (or nearly identical) hollow fiber membranes may be accurately determined using the same graphical technique outlined above. In this case, the total bore side flow of sweeping gas directed through the hollow fiber module can be divided by the number of fibers per module to get the average flow through one fiber. Then, by plotting the variation in concentration of a particular permeate in the effluent sweeping gas as a function of reciprocal bore side flow rates, the permeation coefficient of individual permeating gaseous species may be determined graphically as indicated above. Of course, all of the procedures, limitations, and assumptions described earlier also apply in this situation.

It is understood that other more conventional methods of determining permeability coefficients [e.g., Refs. 13, 20, 25, and 41] are also capable of producing very good results. However, one of the main advantages of the procedure described in this paper is that permeability coefficients can be accurately determined for specific gas species which must experience relatively high fluxes of counterdiffusing secondary sweeping gases. In addition, preliminary experimental studies in our laboratory have indicated that different types of counterdiffusing sweep gases can have a significant effect upon gaseous permeability coefficients. This phenomenon is probably related to a variation in the plasticizing effect in the PFA tubing caused by differences in the physical and chemical nature of the counterdiffusing sweeping gas.[8] In any case, a more thorough and complete knowledge of these effects is important if the process described herein for producing predetermined, reasonably constant, and very low concentration levels of various dopant gases in selected carrier gases is to be used more widely in the future.

CONCLUSION

One of the primary results of this study is an experimentally determined value of the permeability coefficient (K) for the diffusion of oxygen through a membrane made of Teflon–PFA tubing. The actual value of this constant,

determined under the conditions described above, is

$$K = 1.03 \times 10^{-8} \left[cm^3(stp) \ mm \right] \left[cm^2 \ s \ cm \ Hg \right]$$

Other experimental measurements indicated that gaseous permeability coefficients may be highly dependent on, *inter alia*, batch processing differences between the same kind of tubing as well as the type of gas into which the oxygen diffuses. Additional studies designed to further investigate these effects are planned and will be published at a later date.

Another interesting result of this study is a theoretically derived equation, as well as a related graphical technique, which can be used to facilitate the determination of experimental permeability coefficients for other gas/tubular membrane system combinations. At present, it is thought that this may be a new and useful experimental technique and has, therefore, been reported herein.

APPENDIX A

The permeation rate ($\dot{Q}$) of any gas which diffuses through a tubular membrane is given by the following expression[17]:

$$\dot{Q} = \left[2\pi KL(P_{ex} - P_{in}) \right] / \left[\ln(b/a) \right] \tag{3}$$

If all of the variables in eq. (3) stay constant with time, the quantity of gas (Q) which will diffuse through the tubing wall in a time period of t is:

$$Q = \left[2\pi KL(P_{ex} - P_{in})t \right] / \left[\ln(b/a) \right] \tag{4}$$

A very small volume element (ΔV) of an originally pure gas (having dimensions of $\pi a^2 \Delta L$ and passing through the inside of the tubular membrane) will pick up the following incremental quantity (ΔQ) of permeating gas in a very short time period of Δt:

$$\Delta Q = \left[2\pi K \Delta L(P_{ex} - P_{in}) \cdot \Delta t \right] / \left[\ln(b/a) \right] \tag{5}$$

But, in the case of the study described in this paper, P_{ex} was always very much larger than P_{in}. Therefore, the expression above (5) can be simplified by assuming that

$$P_{ex} - P_{in} \approx P_{ex} \tag{6}$$

Equation (5) can then be rewritten as

$$\Delta Q = \left[2\pi K \cdot \Delta L P_{ex} \cdot \Delta t \right] / \left[\ln(b/a) \right] \tag{7}$$

It is also possible to assume that the total quantity of gas (Q_T) which diffuses into the same small volume element (ΔV), as it moves from the inlet end of the gas permeable tubing to the outlet end, is

$$Q_T = \Delta Q(L/\Delta L) \tag{8}$$

where ($L/\Delta L$) is the total number of times that the small volume element (ΔV) picks up ΔQ units of the permeating gas. Combining equations (7) and (8),

$$Q_T = \left[2\pi K \cdot \Delta L P_{ex} \cdot \Delta t (L/\Delta L) \right] / \left[\ln(b/a) \right]$$

or $$\tag{9}$$

$$Q_T = \left[2\pi KL P_{ex} \cdot \Delta t \right] / \left[\ln(b/a) \right]$$

If the small time element of Δt is replaced by $\Delta L/v$, the following expression is obtained:

$$Q_T = [2\pi K L P_{ex}(\Delta L/v)]/[\ln(b/a)] \tag{10}$$

The final impurity concentration ([X], expressed as a mole fraction) which is produced in the original small volume element (ΔV) is given by the following expression:

$$[X] = [2\pi K L P_{ex}(\Delta L/v)]/[\Delta n \cdot \ln(b/a)] \tag{11}$$

where Δn is the quantity of gas (mol) in the original small volume element (ΔV), and

$$\Delta n = (P \cdot \Delta V)/(RT) = (P\pi a^2 \cdot \Delta L)/(RT) \tag{12}$$

Therefore, combining equations (11) and (12), the final impurity concentration in the small volume element (ΔV) leaving the end of the permeable tube (and all successive small volume elements) is

$$[X] = [2\pi K L P_{ex}(\Delta L/v)RT]/[P\pi a^2 \cdot \Delta L \cdot \ln(b/a)] \tag{13}$$

Cancelling the ΔL terms and rearranging slightly yields

$$[X] = [2\pi K L P_{ex}RT]/[P\pi a^2 \cdot v \cdot \ln(b/a)] \tag{14}$$

But, the gas flow through the tube is

$$F_p = A \cdot v = \pi a^2 \cdot v \tag{15}$$

and

$$v = F_p/(\pi a^2) \tag{16}$$

However, the following relationship exists between the actual gas flow (F_p) and the gas flow expressed at standard conditions (F_{stp}):

$$F_p = F_{stp}(P_0/P) \tag{17}$$

where $P_0 = 1.0$ atm.
    Therefore, using (17) in (16) and that result in (14) yields:

$$[X] = [2\pi K L P_{ex}RT]/[P\pi a^2(F_{stp}/\pi a^2) \cdot (P_0/P) \cdot \ln(b/a)] \tag{18}$$

On simplification, (18) may be rewritten as:

$$[X] = [2\pi K L P_{ex}RT]/[F_{stp}P_0 \cdot \ln(b/a)] \tag{19}$$

This completes the derivation of eq. (1) employed earlier in this paper.

APPENDIX B: NOMENCLATURE

a	inner tubing radius
b	outer tubing radius
F_p	actual gas flow within tubing
F_{stp}	gas flow within tubing expressed at 0°C and 1.0 atm
K	permeability constant
L	length of tubular membrane

ΔL very short length of tubular membrane
Δn quantity of "clean" gas (in small volume element) being doped with diffusing impurity gas
P absolute pressure of "clean" gas being doped with a diffusing impurity
P_{ex} external partial pressure of permeating gas
P_{in} internal partial pressure of permeating gas
P_0 a constant = 1.0 atm
Q_T total quantity of gas which diffuses into tubular membrane
$\dot{Q}$ gas permeation rate
ΔQ small quantity of gas diffusing into a small volume element within a tubular membrane
R universal gas constant
t time interval
Δt very short time interval
T absolute temperature
v velocity of gas moving in tubing bore
ΔV small volume element of gas in tubing bore
$[X]$ final impurity concentration expressed as a mole fraction

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