Deconvolution of Permeance in Supported Nanoporous Membranes

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Nanoporous membranes—porous membranes generally having a porosity below 1 nm—have attracted the attention of many researchers because of their potential for technological advances in gas separations and shape selective catalysis (Saracco et al., 1994). Permeation experiments often constitute a significant contribution to the characterization of these membranes. As the dimensions of a pore approach that of the molecule, transport generally becomes extremely sensitive to the molecular dimensions of the probe gas and very high separation factors have been reported for ceramic (Vercauteren et al., 1998), zeolite (Bai et al., 1995), and nanoporous carbon membranes (Rao and Sircar, 1993, Acharya et al., 1997) of this type.

Several researchers (Acharya et al., 1997; Bai et al., 1997; Hayashi et al., 1997) have examined the *driving force normalized flux* or *permeance* π of various molecular probes through these membrane systems

$$\pi = \frac{J_{ss}}{\Delta p} \tag{1}$$

in an attempt to ascertain the effect of molecular dimensions on the overall transport observed through the membrane and thereby obtain information regarding the selective porosity. This parameter is convenient to measure and use since it is often difficult to define the actual thickness of the active membrane layer in these systems. This is especially true for supported nanoporous membranes where a portion of the membrane material resides within the macroporosity of the support and the interface is typically dominated by surface irregularities and cracks (Acharya et al., 1997; Hayashi et al., 1997; Kusakabe et al., 1998). The parameter is also used to describe diffusion over a range of linear transport regimes through these materials from the Knudsen mechanism to coupled adsorption and transport.

Unfortunately, the permeance is an extrinsic parameter that generally contains a convolution of the effects of membrane porosity, active layer thickness, adsorption, and geometric influences. These effects must be isolated and controlled if any meaningful comparison with the observed gas separation factors is to be made as a function of membrane synthesis and permeation conditions. For example, Hayashi and co-workers (1997) attempted to correlate the observed permeance of gases through a series of carbonized polyimide membranes with the kinetic diameter of the molecular probe for different oxidation temperatures. However, in the absence of knowledge concerning membrane thicknesses, adsorption, or variations in the porosity—all of which may be strong functions of synthesis temperature—a meaningful comparison of membranes in this way is impossible.

Conceptually, it has been thought that the permeances of molecular probes through molecular sieving media arise from the transport of an adsorbed phase which migrates along the surface in the direction of the overall driving force (Ruthven and Karger, 1992). This surface transport has been described using the adsorbed phase concentration gradient as the driving force and by defining a surface diffusion coefficient. Barrer and co-workers (1950) asserted that this surface flow occurs in parallel with Knudsen transport. The total flow through the medium was deconvoluted by first measuring the flow of a ‘‘nonadsorbing’’ reference gas. The Knudsen contribution made by any other nonadsorbing gas was calculated using this flux and the known scaling of the Knudsen diffusivity with molecular weight. The difference between the total flow and the so-called gas-phase flow was attributed to the surface flux. It is now generally recognized that this ‘‘calibration gas’’ method is flawed when applied to microporous media. For example, using this method, researchers have observed that the surface flow contribution can apparently be negative and that the Knudsen or gas-phase component can appear to be activated with an Arrhenius-like temperature scaling (Nicholson and Petropoulos, 1973; Shindo et al., 1983).

The current consensus is that transport through microporous, or, more appropriately, nanoporous systems, is characterized by surface diffusion almost exclusively in the low-temperature limit and an ‘‘activated gas-phase’’ diffusion at higher temperatures (Nicholson and Petropoulos, 1973, 1979, 1981; Shelekin et al., 1995). The apparent activation

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energy for this so-called gas-phase diffusion decays to zero in the limit of high temperature and the diffusion coefficient approaches the conventional Knudsen value. Little is understood about the transition region between these two mechanisms, and it is doubtful that it can be represented as merely a sum of gas and adsorbed-phase contributions as Barrer has done (Nicholson and Petropoulos, 1981).

In light of these observations, Shelekhin et al. (1995) have examined adsorption and activated diffusion through microporous glass membranes ($d_{\text{pore}} = 1.5 \pm 0.5$ nm) and have defined the concept of an *iso-concentration temperature*. At this temperature for a given molecular probe in a particular porous medium, the concentrations of the gas and adsorbed phase contribute equally to the total concentration in the system. The authors reasoned that, at temperatures above this point, transport takes place almost exclusively by activated gas-phase diffusion. Below this point, flow of an adsorbed phase dominates the transport. For He and H_2, this temperature was approximately 118 and 143 K, respectively, while, for N_2, O_2, and CO_2, these temperatures were considerably higher at 283, 328 and 473 K, respectively. Despite the relatively large values reported for this temperature for N_2 and O_2 in the glass membrane, these molecular probes were modeled using exclusively a gas-phase driving force. It was also noted by the authors that an increase in temperature by as little as 20 K above the iso-concentration point resulted in an order of magnitude decrease in the adsorbed-phase concentration indicating that the transition region can be quite narrow. Nicholson and Petropoulos (1973, 1979, 1981) defined a temperature normalized adsorption potential ($U_o =$ adsorption energy/kT) and showed that with increasing U_o, the total flux through a porous system relative to the Knudsen predicted value generally passes through a minimum. The total flow exceeds that predicted by the Knudsen equation at higher values of U_o as the flow becomes dominated by the transport of this adsorbed phase. An increase in the kinetic diameter of the adsorbate relative to the pore width shifts the location of this minimum to lower values of U_o.

The purpose of this article is to introduce a technique that can be used to dissect the relative contributions of the overall permeances through molecular sieving membranes. By examining the transient response of an initially evacuated membrane to a step change in pressure loading at its boundary, information concerning the intrinsic diffusivity of the molecular probe can be obtained (Daynes, 1920; Ruthven and Karger, 1992). For linear systems, this diffusivity is independent of any adsorption effects and can be used to measure the Henry's law adsorption constants from the permeation data. In this way, the method can also distinguish between flow induced primarily by a gas phase or an adsorbed phase driving force, and, at lower values of U_o, as defined above, can be used to define an active layer thickness of the membrane.

Model Development

It is generally accepted that, at infinite temperature, the permeances of all molecular probes through microporous media should approach the Knudsen values (Shelekhin et al., 1995; van de Graaf et al., 1999). On the other hand, in the low-temperature limit one anticipates that flow will take place almost entirely in an adsorbed phase. Nicholson and Petropoulos (1981) point out that, physically, the distinction between gas and adsorbed phases within microporous media is completely arbitrary. When activated diffusion is described by a gas-phase concentration gradient, however, the flux should be proportional to a linear driving force and should scale identically for all molecular probes in this regime. On the other hand, if the flow is dominated by that of an adsorbed phase in the infinite dilution limit, then the driving forces for each molecular probe will scale differently, and will be proportional to the particular value of the Henry's law constant. Adopting the notation of Nicholson and Petropoulos (1979, 1981), one can identify these two limiting cases using the potential U_o. For a given system, when the temperature of permeation is large enough such that U_o is vanishingly small, the former mechanism is controlling. Conversely, at lower temperatures, the latter mechanism is expected to dominate.

At the lower temperature limit, for a particular molecular probe in a given porous medium, one anticipates that the permeation of an adsorbed phase dominates the flux. Because the molecular probes at the conditions considered in this work display experimentally a flux that is linearly related to the bulk pressure driving force (see the Experimental Studies section), the adsorbed phase must be in the Henry's law regime. Taking this adsorbed-phase concentration to be in equilibrium with and proportional to the bulk-phase concentration ($q = Kc$), we can write the following description of isothermal transport through an initially evacuated membrane of thickness δ (μm), subject to a step change in ideal gas-pressure loading p_o

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2} \qquad \begin{array}{l} q(t, x=0) = q_o = K\dfrac{p_o}{RT} \\ q(t, x=\delta) = 0 \\ q(t=0, x) = 0 \end{array} \tag{2}$$

The flux of this adsorbed phase through a cross section of the membrane at $x = x_o$ is then related to the bulk-phase partial pressure via

$$J(t, x = x_o) = -\frac{D\rho K}{RT\epsilon}\frac{\partial p}{\partial x}\bigg|_{x = x_o} \tag{3}$$

where ρ and ϵ are the density (kg/m^3) and porosity (m^3 void space/m^3 membrane material) of the membrane material. This formulation is similar to that used in chromatographic studies of transport in nanoporous carbon in the limit of Henry's law adsorption (Kawazoe et al., 1974; Chihara et al., 1978).

The solution to the above expression for the total permeate flow through the membrane as a function of time is analogous to the solution presented by Daynes (1920)

$$A\int_0^t J(t')\,dt' = \frac{AD\rho Kp_o}{\epsilon\delta RT}t - \frac{A\delta\rho Kp_o}{6\epsilon RT} - \frac{2A\delta\rho Kp_o}{\pi\epsilon RT} \times \sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left\{\frac{-n^2\pi^2 Dt}{\delta^2}\right\} \tag{4}$$

This permeate flow becomes asymptotic to a linear function as $t \rightarrow \infty$

$$A\int_0^t J(t')\,dt' \cong \frac{AD\rho Kp_o}{\epsilon RT\delta}\left(t - \frac{\delta^2}{6D}\right) = AJ_{ss}(t-\tau) \qquad (5)$$

Measuring the slope (AJ_{ss}) and time axis intercept τ of this response yields direct measures of the following groups of parameters

$$AJ_{ss} = \frac{AD\rho Kp_o}{\epsilon RT\delta} \qquad (6)$$

$$\tau = \frac{\delta^2}{6D} \qquad (7)$$

It follows that a plot of the quantity $(6AJ_{ss}\tau RT)$ vs. p_o should be linear

$$6J_{ss}\tau RT = \frac{\delta\rho K}{\epsilon}p_o \qquad (8)$$

and should provide a measure of the thickness of the membrane δ times an apparent dimensionless adsorption constant $K\rho/\epsilon$. The thickness-normalized diffusivity can be obtained from τ as

$$\frac{D}{\delta^2} = \frac{1}{6\tau} \qquad (9)$$

Alternatively, if the temperature of permeation is such that U_o is small, then diffusion through the medium will be dominated by gas-phase flow and will approach the Knudsen limit. The distinction for transport in this regime is that the bulk-phase pressure gradient drives transport across the membrane with no attenuation due to adsorption. Reformulating the problem above and restating the boundary conditions for a "nonadsorbing" molecule yields a mass balance on the gas phase

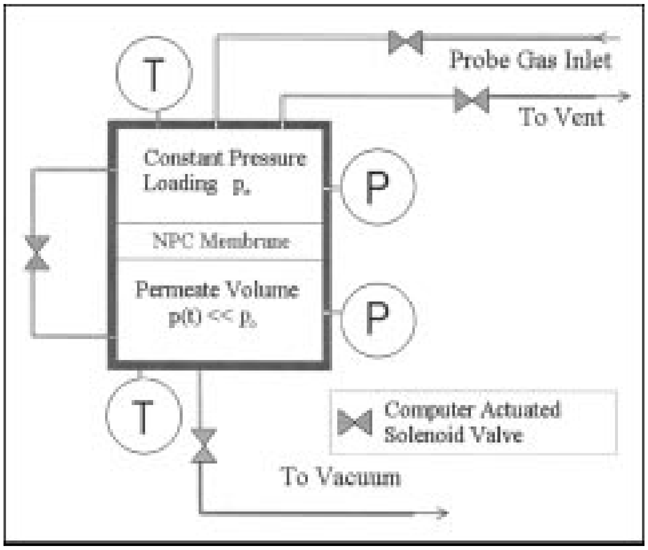

Figure 1. Experimental apparatus used to generate and monitor the transient response of an ideal gas molecular probe through an initially evacuated membrane.

T: thermocouple placed at the membrane surface; P: pressure transducer.

$$\frac{\partial p}{\partial t} = D_g\frac{\partial^2 p}{\partial x^2} \qquad \begin{array}{l} p(t, x=0) = p_o \\ p(t, x=\delta) = 0 \\ p(t=0, x) = 0 \end{array} \qquad (10)$$

Solving Eq. 10 for the net permeate flux as above yields the solution of Daynes (1920)

$$A\int_0^t J(t')\,dt' = \frac{AD_g p_o}{RT\delta}t - \frac{A\delta p_o}{6RT} - \frac{A2\delta p_o}{\pi RT} \times \sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left\{\frac{-n^2\pi^2 D_g t}{\delta^2}\right\} \qquad (11)$$

Again, taking the limit as $t \rightarrow \infty$ allows one to measure the time axis intercept and the steady-state flux as given by the slope and intercept of the asymptote. Solving for the effective thickness δ and the gas-phase diffusivity D_g

$$\delta = \frac{6J_{ss}\tau RT}{p_o} \qquad (12)$$

$$D_g = 6\tau\left(\frac{J_{ss}RT}{p_o}\right)^2 \qquad (13)$$

Plotting $(6AJ_{ss}\tau RT)$ vs. p_o for various molecular probes, both Eqs. 12 and 13 predict that for transport dominated by gas-phase flow, the linear curves should overlap with a slope equal to the effective thickness of the membrane. Alternatively, adsorbing molecular probes in the Henry's law regime should exhibit slopes that vary with the value of the adsorption constant, as predicted by Eq. 8. The dominance of either regime is a strong function of the adsorption properties of the molecular probe, the permeation temperature, and the pore-size distribution of the porous medium. While there is no established formalism for representing the convolution of these regimes, comparing the transient responses of permanent gases using Eqs. 6–7 and 12–13 in this way, one can identify transport approaching either limit. The methodology described above can yield a more rigorous description of transport through nanoporous membranes than can a simplistic permeance model as is ubiquitous in the literature.

Experimental Studies

Figure 1 shows the experimental apparatus for generating and recording the transient response of a molecular sieving membrane to a step change in ideal gas pressure at its boundary. At a time $t = 0$, the ideal gas (from Keen, 99.99% pure) is introduced to the top of an initially evacuated membrane at a pressure p_o. The permeate volume bounding the bottom of the membrane is sealed from vacuum at this time and the subsequent rise in pressure is used to evaluate the instantaneous derivative of the time dependent flux through the membrane

$$\frac{V_{pc}}{RT}\left(P(t)-P_{\text{int}}\right)=A\int_0^t J(t')\,dt' \tag{14}$$

where V_{pc} is the volume of the permeate chamber (m^3), P_{int} is the initial pressure in the chamber at $t=0$ (Pa), and A is the area of the membrane (m^2). This pressure is measured using an MKS Baratron pressure transducer (0–1,000 torr range) and is recorded using an interfaced PC which also controls the start and duration of the experiment via electronically actuated solenoid valves. If the pressure rise in this volume is not permitted to exceed a minimum value, $P(t)<4$ torr, the driving force across the membrane is approximately equal to the pressure loading. The rate of change of the pressure rise in Eq. 14 increases from zero initially at $t=0$ to a constant rate as time proceeds. The time needed to achieve this steady-state pressure rise and steady-state flux from Eq. 3 varies dramatically with the choice of molecular probe. After the transient response and steady-state flux are recorded, the membrane is evacuated for a period equal to several times this characteristic time scale for permeation before the experiment is repeated. In this way, the transient flux $J(t)$ at any pressure loading p_o can be monitored until the steady-state flux J_{ss} is observed.

The method was demonstrated using a series of stainless steel supported nanoporous carbon membranes; the synthesis of these membranes has been described elsewhere (Acharya et al., 1997; Acharya and Foley, 1999). Figure 2 demonstrates the measurement of the transient response of a stainless steel supported nanoporous carbon membrane (11.4 cm^2 area, 100 mg carbon deposition, 673 K pyrolysis temperature) to various nitrogen pressure loadings. The time axis intercept is obtained by measuring the slope of the response well after the initial period of transient flow ($t \approx 100\ \tau$) and extrapolating this asymptote to the time axis. This intercept is independent of the pressure driving force for concentration-independent diffusion coefficients.

For ideal gas molecular probes at ambient temperatures and moderate pressures, the steady-state flux is observed to be linearly related to the driving force pressure difference p_o through molecular sieving membranes (Acharya et al., 1997; van de Graaf et al., 1999). Figure 3 demonstrates this experimentally for the carbon membrane used in Figure 2. The linearity of the flux vs. pressure indicates that the transport adheres to a linear driving force model, and that adsorption onto the membrane surface, if present, must be in the Henry's law regime.

Results and Discussion

Figure 4 shows the transient responses of He, Ar, N$_2$, and O$_2$ produced from various step changes in pressure at the boundary of a carbon molecular sieving membrane (11.4 cm^2 area, 100 mg of carbon, synthesized at 573 K). The extrapolated intercepts are independent of the pressure within error as shown. The time scale of the experiment changes significantly with the molecular probe employed, and the intercept is most accurately measured at longer time scales. Figure 5

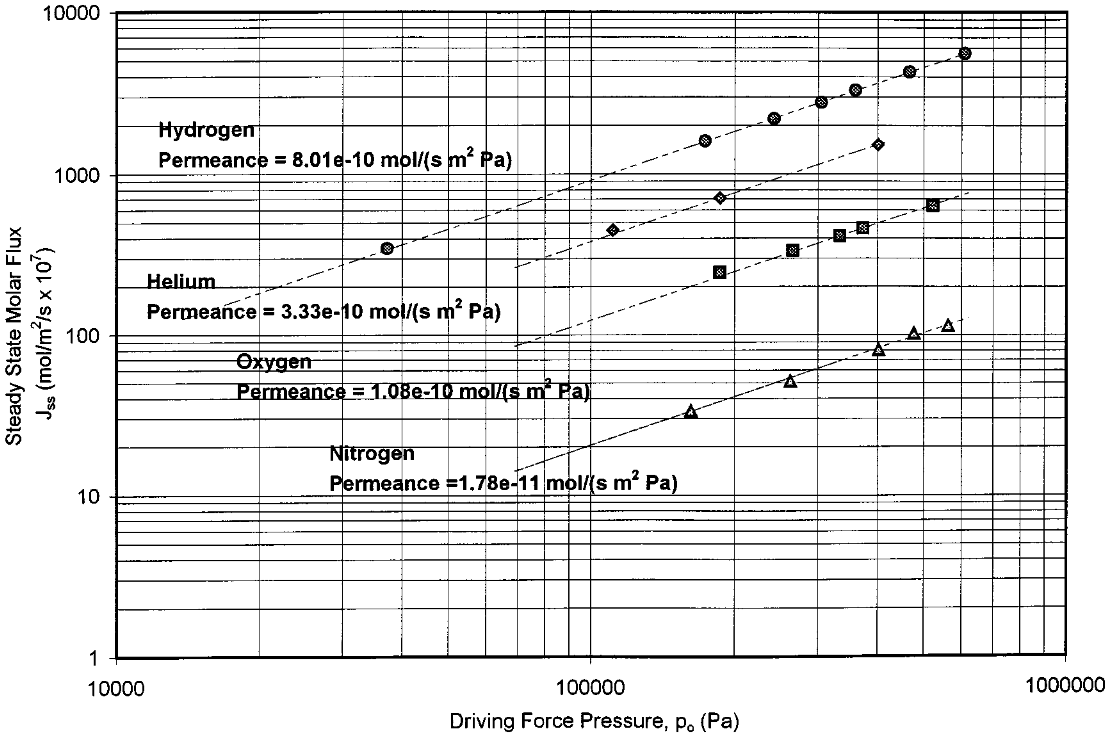

Figure 2. Steady-state fluxes of ideal gases through a 100 mg stainless steel supported nanoporous carbon membrane synthesized at 673 K.

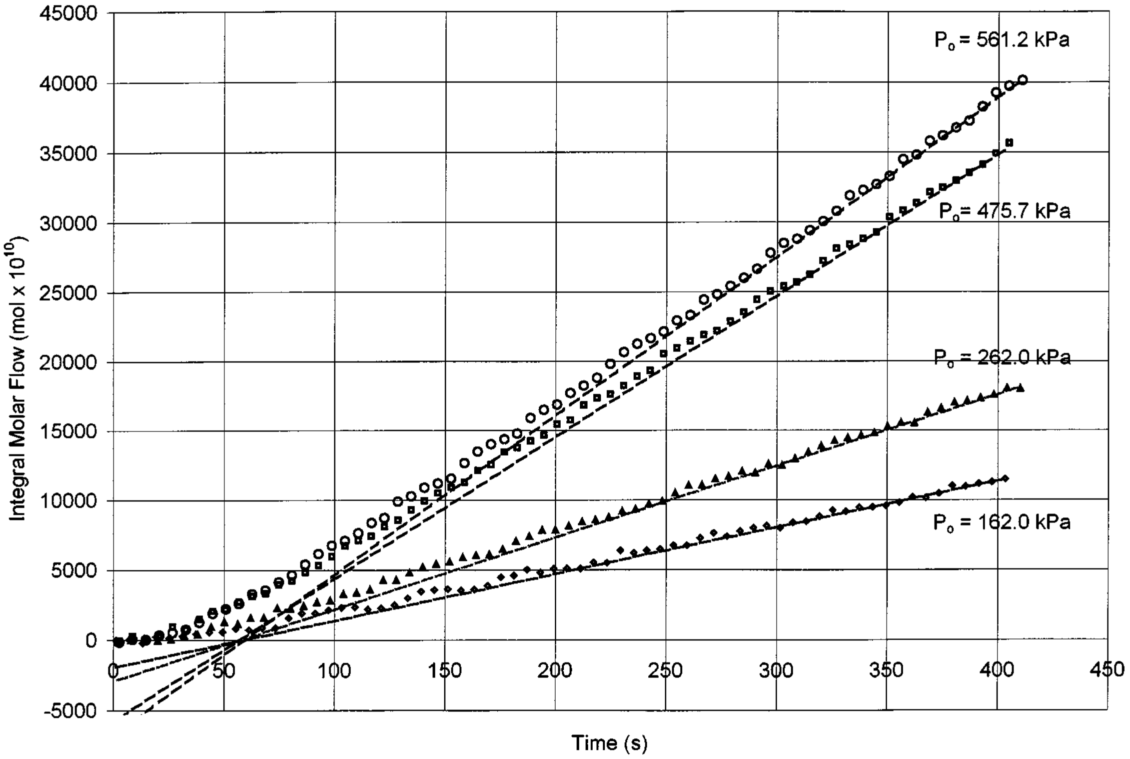

Figure 3. Demonstration of the measurement of the time axis intercept through a nanoporous carbon membrane (100 mg, 673 K) using nitrogen permeation.

shows a plot of $(6J_{ss}\tau RT)$ vs. p_o for these gases, and the curves are linear as predicted by Eqs. 8 and 12. The fact that these curves do not coincide is a clear indication that the driving force for some of the molecular probes is dominated by the adsorbed phase. This result is contrary to that of Shelekhin et al. (1995) who found that permeation of permanent gases through microporous glass membranes ($d_{\mathrm{pore}} = 1.5 \pm 0.5$ nm) was accurately modeled using a gas-phase concentration gradient and modified Knudsen equation. The average pore size of molecular sieving carbons, however, is narrower ($d_{\mathrm{pore}} = 0.5$ nm; Mariwala and Foley, 1994) than that for microporous glass, and it is certainly reasonable to expect that this decrease in mean pore size shifts the values of U_o dramatically thereby changing the dominant transport regime.

One anticipates that He adsorption on the membrane will be negligible at 300 K and pressures near ambient. Using Eqs. 12 and 13 for the He data in Figure 5 yields an effective thickness of 3.8 μm and a diffusivity of 2.46e-12 m^2/s.

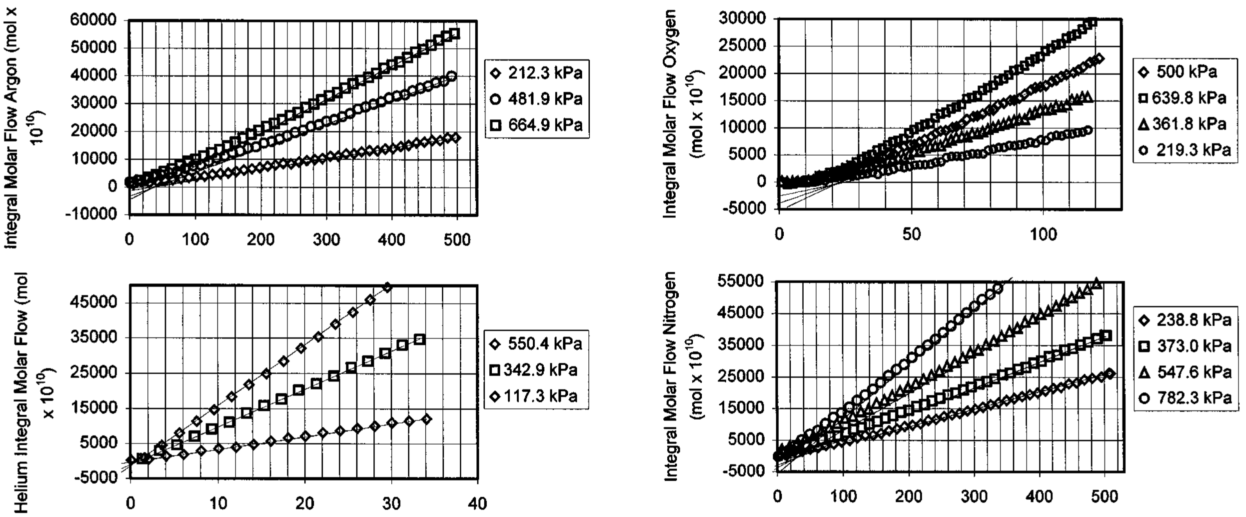

Figure 4. Transient responses of a 140 mg carbon membrane synthesized at 500 C for various molecular probes.

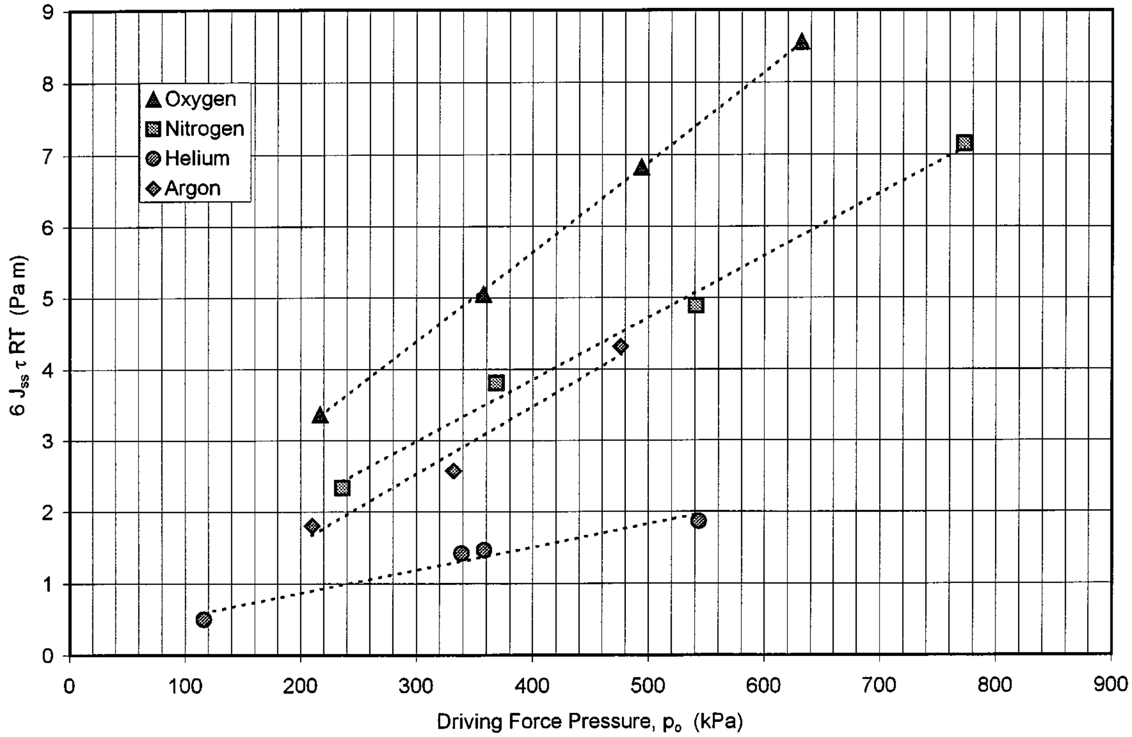

Figure 5. Plot of $(6 J_{ss} \tau RT)$ vs. the membrane pressure loading p_o.

This thickness is reasonable as it compares fairly well to the estimate of 8.2 μm assuming that the 14 mg deposition of the last carbon layer contributes solely to this active layer thickness and assuming a carbon density of 1.5 g/cm^3. The thickness also agrees to within a factor of five with that obtained from microscopy performed on typical membrane cross sections (Acharya et al., 1997; Chen and Yang, 1994). The He diffusivity, if it were assumed to be within the Knudsen regime, can be used to calculate an effective Knudsen pore diameter of 0.59 nm. This value is remarkably close to the well established mode of the pore side distribution of about 0.5 nm for (poly)-furfuryl alcohol carbon molecular sieves (Mariwala and Foley, 1994.) Although transport of He in pores of this average diameter has been described as being activated, the measured apparent activation energy is so low that it is difficult to state unequivocally which mechanism of diffusion is dominant. Furthermore, some researchers have observed that He may indeed adsorb on nanoporous surfaces, albeit weakly, and have argued for He surface flow at room temperature through very narrow pore materials (van de Graaf et al., 1999).

Table 1. Comparison of Length Normalized Diffusivities and Dimensionless Adsorption Constants for Granular Nanoporous Carbon and Nanoporous Carbon Membrane Used in This Work*

Reference	Carbon Type	D/δ^2		$K\rho/\epsilon$	
		O_2	N_2	O_2	N_2
Ruthven and Karger (1942)	Bergbau	3.70e-3	1.10e-4	10.5	10.5
Knoblauch	Bergbau	1.70e-4	7.00e-6	9.3	8.9
Chihara et al. (1978)	Takeda	1.90e-4	3.40e-2	12	12
Chihara et al. (1978)	Takeda	4.50e-3	1.10e-3	5	5
Dominguez	BOC	8.20e-3	1.90e-4	9.4	10.2
This work	PFA	7.03e-3	5.13e-3	3.7	2.4

*Ruthven and Karger (1992).

Table 1 compares the thickness normalized diffusivities and dimensionless infinite dilution adsorption constants for O_2 and N_2 as measured using Eqs. 8 and 9 to values obtained by gravimetric and chromatographic methods performed on granular carbons by various researchers (Ruthven and Karger, 1992). While these values are expected to be a function of the type and synthesis conditions of carbon, the comparison reveals fairly good agreement between the two geometries. The ratio of the adsorption constants for O_2 and N_2, measured as the ratio of the slopes in Figure 5, is 1.53 O_2/N_2 and is consistent with ratios appearing in the literature for various nanoporous carbons (Ruthven and Karger, 1992), as well as polymeric membranes (Singh and Koros, 1996), the values of which range between 0.7 to 2. One also notes that the adsorption constants for Ar and N_2 are nearly identical. This has also been observed by Chihara et al. (1978) for molecular sieving carbon and Golden and Sircar (1994) for silicalite.

This analysis breaks down for a strongly adsorbing gas where the adsorbed phase concentration is outside of the Henry's law limit. For example, one observes that for CO_2 at 298 K, the time axis intercepts are seen to be highly pressure dependent (Figure 6). This is a clear indication that the intrinsic diffusivity is no longer concentration independent and that exact values for the adsorption constant and the intrinsic diffusivity for CO_2 cannot be obtained from Eq. 8. It is qualitatively evident from Figure 6 that the CO_2 ($\sigma = 0.394$ nm)

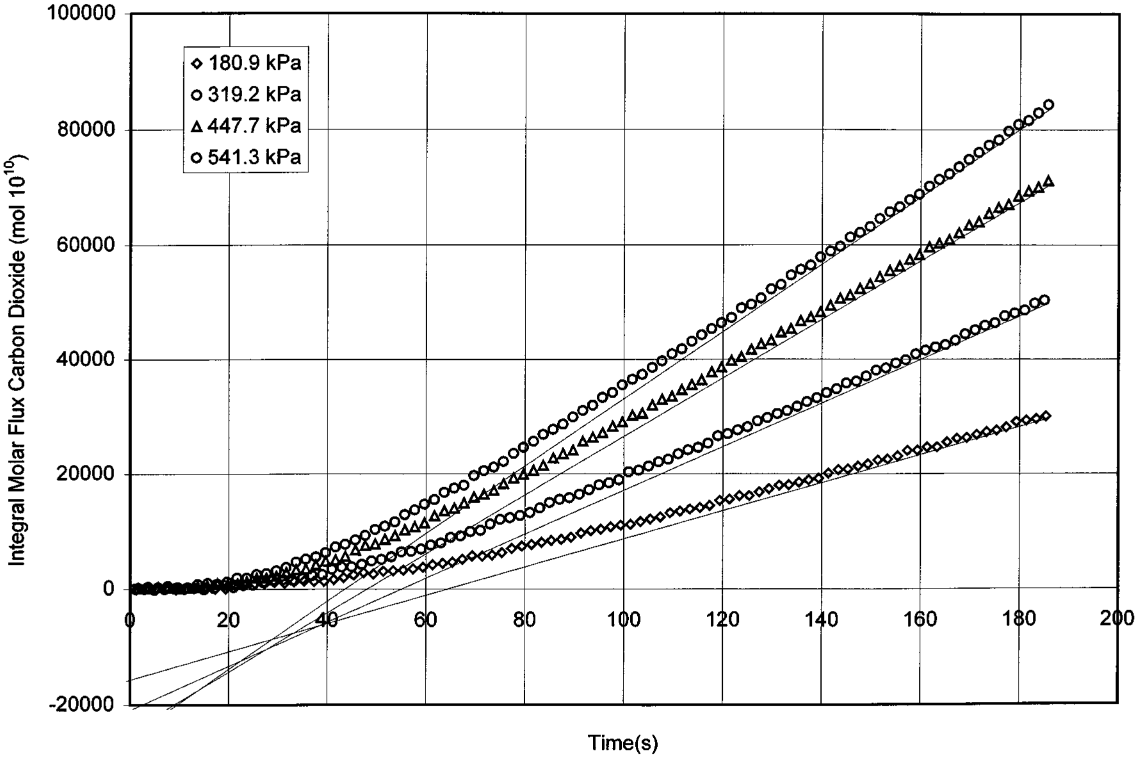

Figure 6. Observed transient response of CO_2 through a 140 mg carbon membrane synthesized at 500 C.

"permeance" is higher than that for O_2 ($\sigma = 0.346$ nm) or N_2 ($\sigma = 0.380$ nm) for carbon membranes because of its stronger adsorption; it is not because it may possess a slightly smaller cross section than O_2 as implied by some authors (Kusakabe et al., 1998). Rather, the effect of CO_2 adsorption represents a much greater contribution to its permeance than for the other permanent gases considered in this note. This observation is supported by the fact that for CO_2, the time axis intercepts at equivalent pressure loadings are greater than O_2, N_2 and Ar, indicating that it possesses a smaller intrinsic diffusivity.

Conclusions and Future Work

The method outlined in this note is a simple yet powerful alternative to describing transport in these systems using a single parameter—the permeance—which contains the effects of membrane properties, as well as the adsorption potential. The method can be used to distinguish gas flow approaching Knudsen streaming from the dominance of surface flow in the limit of infinitely dilute adsorption. If conditions are identified where the permeation of a molecular probe is indeed dominated by a gas-phase driving force, the effective thickness of the membrane is easily calculated.

Considerably more insight may be gained by using the above methodology to study permeation over a range of temperatures. In particular, apparent heats of adsorption and activation energies are easily discernable by examining the temperature behavior of the adsorption constants K and intrinsic diffusivities D. Examining the temperature effects of He flow will provide a test of our assumption of negligible He adsorption on the membrane above 296 K. It should be noted, however, that as the intrinsic diffusivity increases with temperature, the time axis intercept of the experiment decreases reciprocally. At small values, this parameter becomes more difficult to measure accurately and this may limit the investigation of temperature-dependent transport through the membrane over large changes in temperature.

Acknowledgments

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Notation

c = gas-phase concentration of a pure gas, mol/m^3
d_{pore} = mean pore diameter, nm
D_g = observed diffusivity from gas phase flow, m^2/s
D_s = adsorbed phase surface diffusivity, m^2/s
$J(t)$ = transient flux of the membrane exiting the permeate boundary, mol/m^2/s
J_{ss} = steady-state flux through the membrane, mol/m^2/s
k = Boltzman constant, J/K
K = apparent Henry's law adsorption constant, m^3 adsorbed phase/kg membrane
p_o = constant pressure loading applied to the boundary of a membrane at $t = 0$, Pa
$p(t)$ = transient pressure rise of the permeate chamber, Pa
q = surface phase loading of molecular probe, mol/kg
R = ideal gas constant, J/(mol K)
t = time of permeation, s
T = temperature of permeation, K
x = diffusional coordinate, m

τ = time axis intercept of the integral molar flux, s
σ = kinetic diameter of molecular probe, m

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