SINGLE-COMPONENT MASS TRANSFER ACROSS A POROUS MEMBRANE

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The experiment described in this paper deals with the study of single-component gas diffusion across a meso/macro-porous membrane. This work allows not only for the introduction of important mass-transfer concepts, but also for an initiation to separation membrane technology.

This experiment reflects the basic philosophy of our department at the University of Porto concerning undergraduate laboratories: it is pedagogically interesting, setup and maintenance are relatively inexpensive, and the operation is safe and environmentally friendly.

THEORETICAL BACKGROUND

In single-component gas flow across a porous membrane, three transport mechanisms can be considered:[1-4] Knudsen flow, viscous flow, and surface diffusion along the pore walls. The pore diameter mainly determines whether transport within the gas phase is characterized by Knudsen or viscous flow. Surface diffusion is dependent on the tendency of the diffusing species to adsorb on the pore walls.

Knudsen flow is dominant when the pore diameter is of the order of the molecular mean free path. Collisions between molecules and the pore walls are therefore very frequent, more so than molecule-molecule collisions. This mechanism therefore accounts for all the axial momentum loss. Based on basic gas kinetic theory, the following result can be derived for the molar flux of a species diffusing across a membrane under a pressure difference $P_h - P_\ell$:[1,5]

$$N_k = \frac{\varepsilon}{\ell t}\frac{D_k}{RT}\left(P_h - P_\ell\right) \tag{1}$$

where $D_k = \frac{2}{3} r_p \sqrt{\frac{8\,RT}{\pi M}}$

From Eq. (1), the ratio of the single-component fluxes of two different gases (for the same membrane and pressure drop) is given by

$$\frac{N_{k,i}}{N_{k,j}} = \sqrt{\frac{M_j}{M_i}} \tag{2}$$

It is interesting to note that relationship 2 is not exclusive to the Knudsen regime, but can be generalized to bulk diffusion under isobaric conditions—Graham's relation.[1]

On the other hand, for wider pores, inter-molecular collisions predominate. Molecule-wall collisions still take place and lead to loss of axial momentum (*i.e.,* pressure drop), but they are a consequence of a series of molecule-molecule collisions. This can then be treated as a Poiseuille flow problem, leading to[1,5]

$$N_v = \frac{\varepsilon}{\ell\tau}\frac{r_p^2}{8\,\mu RT}\frac{\left(P_h + P_\ell\right)}{2}\left(P_h - P_\ell\right) = \frac{\varepsilon}{\ell\tau}\frac{r_p^2}{16\,\mu RT}\left(P_h^2 - P_\ell^2\right) \tag{3}$$

Knudsen diffusion presents a selective character that is absent in viscous flow. The Knudsen diffusivity (D_k) is inversely proportional to the square root of molecular weight, while on the other hand viscous flow depends on the viscosity (μ), which is much less sensitive to the nature of the gas.

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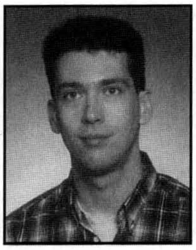

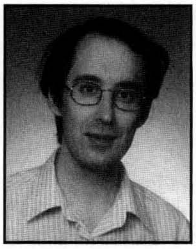

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Both transport processes, Knudsen and viscous, may have a significant contribution for a certain system. This situation can be described by combining Eqs. (1) and (3) in a parallel arrangement[1]

$$N = \frac{\varepsilon}{\ell\tau}\frac{1}{RT}\left(D_k\left(P_h - P_\ell\right) + \frac{r_p^2}{16\,\mu}\left(P_h^2 - P_\ell^2\right)\right) \tag{4}$$

The ratio of fluxes for two different gases now becomes

$$\frac{N_i}{N_j} = \frac{D_{k,i} + D_{v,i}\left(1 + P_h / P_\ell\right)}{D_{k,j} + D_{v,j}\left(1 + P_h / P_\ell\right)} \tag{5}$$

where D_v is defined as $D_v = P_\ell r_p^2 / 16\mu$.

EXPERIMENTAL SETUP

A membrane permeation module was built (see Figure 1). Six PVDF (poly(vinylidene fluoride)) hollow fibers ($7.3\text{x}10^{-4}$ m ID, $1.2\text{x}10^{-3}$ m OD, and $2.6\text{x}10^{-1}$ m length), provided by GKSS Geesthacht (Germany), were assembled inside a transparent tubular shell. These fibers have no selective dense film. They present macro and mesoporosity and are used as a mechanical support layer in gas separation membranes.

The gas feed enters the bore side of the fibers at one end of the module. Since the other end is closed, all gas permeates through the walls and flows along the shell counter currently.

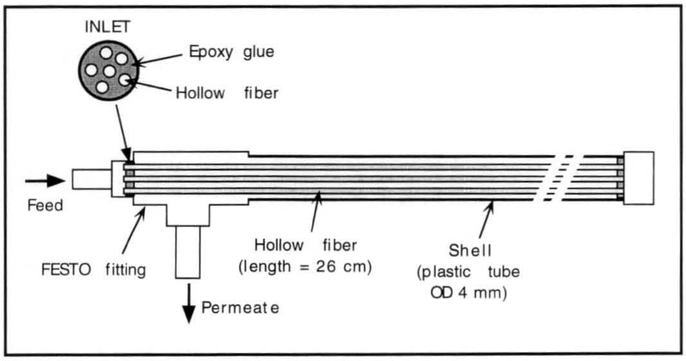

Figure 1. *Sketch of the membrane module.*

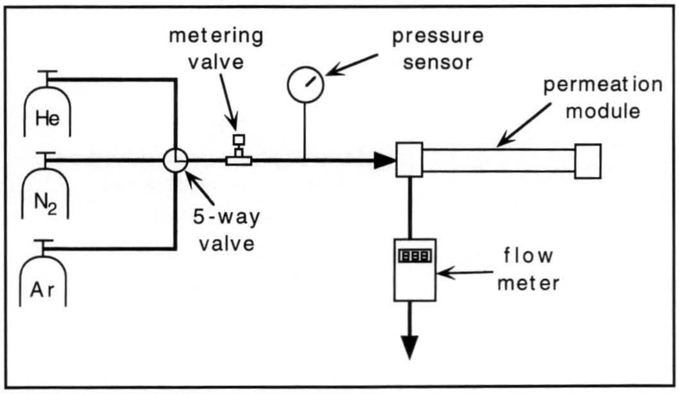

Figure 2. *Sketch of the experimental setup.*

The entire experimental setup is shown in Figure 2. Three gases were studied: He, N_2, and Ar. Other possible choices, like O_2, H_2, or Xe, were eliminated due to their hazardous nature or higher cost. A metering valve was used to regulate the pressure at the module inlet, which was measured with a pressure sensor (0 - $1\text{x}10^5$ N/m^2 relative pressure range, 10^3 N/m^2 resolution). The permeate flow rate was measured with a J&W Scientific ADM2000 flow meter (0 - 1000 sccm).

The outlet pressure at each gas bottle was set at $1.5\text{x}10^5$ N/m^2 (relative), and the metering valve was used to select the module inlet pressures between $0.1\text{x}10^5$ and $1\text{x}10^5$ N/m^2 (relative) in $0.1\text{x}10^5$ N/m^2 intervals.

The experiments reported in this paper were performed at T = 20°C and $P_\ell = 1.011\text{x}10^5$ N/m^2.

DATA TREATMENT AND DISCUSSION OF RESULTS

For this experiment, students were asked to

- *Determine the single-component permeabilities of the three gases*
- *Identify the intra-porous flow regime*
- *Attempt to estimate the average pore radius of the membrane*

The surface diffusion can be neglected in this system since the gases adsorb very little on the polymeric membrane. Thus, only Knudsen and viscous flow must be considered. According to Eqs. (1) and (3), only for Knudsen flow is the flux a linear function of the inlet pressures, or in other words, the effective permeability (defined as $L=N/(P_h - P_\ell)$ is independent of pressure. Plots of the measured flow rates (F) as a function of $P_h - P_\ell$ are shown in Figure 3.

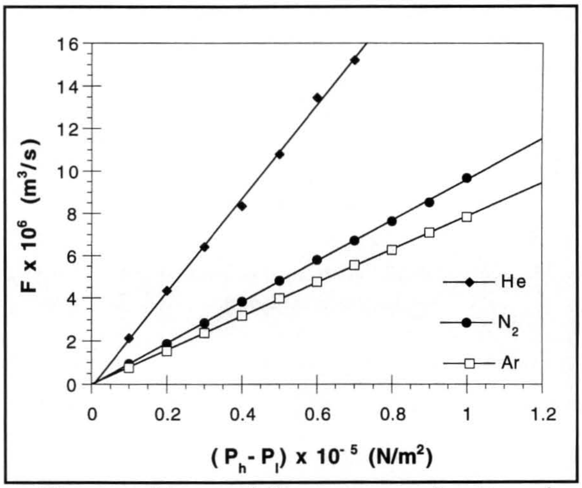

Figure 3. *Measured flow rates as a function of pressure drop for Helium, Nitrogen, and Argon.*

The permeabilities for each gas can be computed directly from the slopes of the straight lines and, as expected, helium, the smallest molecule, shows the highest value.

Since N vs. $(P_h - P_\ell)$ follows a linear relationship, students are led, at this point, to conclude prematurely that viscous flow does not play a role in this system. But the conclusive test consists in checking whether Eq. (2) is verified. The computed flux ratios (averaged over the studied pressure interval) are shown in Table 1 and are compared to the values predicted for Knudsen flow by Eq. (2).

Any error higher than 10% must never be dismissed a priori by an engineer. Therefore, students should find it worthwhile to check for the existence of a not-negligible viscous flow contribution. This can be done efficiently using Eq. (4), rewritten as[5]

$$\frac{NRT}{(P_h - P_\ell)v_k} = \frac{\varepsilon}{\ell\tau} r_p + \frac{\varepsilon}{\ell\tau} \frac{r_p^2}{16} \frac{(P_h + P_\ell)}{\mu v_k} \qquad (6)$$

where $v_k = \frac{2}{3}\sqrt{\frac{8\,RT}{\pi M}}$.

A plot of $NRT/(P_h - P_\ell)v_k$ as a function of $(P_h + P_\ell)/\mu v_k$ will be a straight line, with the slope and the intercept depending only on the unknown parameters r_p and ε/τ. In other words, the data points corresponding to different gases all fall on the same line. Notice also that in the absence of viscous flow, the plot would be a horizontal line.

Figure 4 shows the plot of our data using Eq. (6). The necessary gas properties data is given in Table 2. From the plot, one sees that an analysis based on the results for N_2 and Ar alone would be inconclusive due to data dispersion and to the similar properties of the two gases. Once he is considered, however, it becomes evident that the line is not horizontal, and therefore viscous flow must be considered in addition to Knudsen flow.

The value of r_p computed from the linear regression is 84±6 nm (for a 95% confidence interval). Using this value in Eq. (5), the theoretical flux ratios can be recomputed. The results, shown in Table 3, confirm that the model with combined Knudsen and viscous flows describes the experimental data significantly better.

Finally, the relative contributions of each flow process can be computed for each gas

$$\frac{N_k}{N_k + N_v} = \frac{D_k}{D_k + D_v(1 + P_h / P_\ell)} \qquad (7)$$

The results are shown in Table 4.

We expected that helium would show the greatest contribution from Knudsen flow since this molecule has the lowest molecular weight and hence the highest Knudsen diffusivity (D_k).

CONCLUSIONS

The experiment described here is simple to set up and not

TABLE 1
Experimental (Average) and Theoretical (Eq. 2) Flux Ratios

Gases	N_i/N_j exp.	N_i/N_j Knudsen	Error%
He/N_2	2.27	2.65	17
He/Ar	2.74	3.16	15

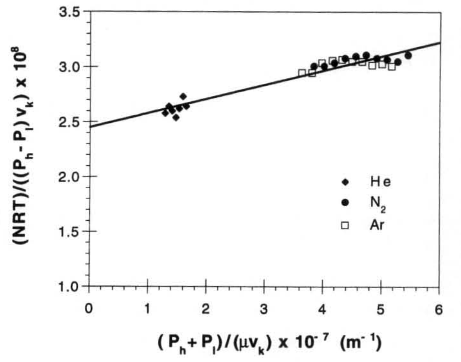

Figure 4. Experimental data points plotted according to Eq. (6).

TABLE 2
Molecular Weights and Viscosities at 20°C[6] for the Studied Gases

Gases	M (g mol^{-1})	μ (Kg m^{-1} s^{-1})
He	4.003	1.98×10^{-5}
N_2	28.02	1.76×10^{-5}
Ar	39.94	2.22×10^{-5}

TABLE 3
Experimental (Average) and Theoretical (Eq. 5) Flux Ratios

Gases	N_i/N_j exp.	N_i/N_j Knudson+viscous	Error%
He/N_2	2.27	2.32	2.2
He/Ar	2.74	2.79	1.8

TABLE 4
Average Percentage of Knudsen Flow in the Pressure Interval Studied (from Eq. 7)

Gases	% Knudsen flow
He	92
N_2	80
Ar	81

expensive. Data collection is also quite unelaborate and students can easily perform the necessary calculations during class time. Besides allowing for a first contact with separation membrane technology, the experiment provides insight into intra-pore gas-phase transport mechanisms. The sequence of calculations necessary for the result analysis should be quite intuitive for the students and help in the assimilation of the theoretical concepts.

For the particular system studied here, evidence was found of viscous flow coexisting with Knudsen diffusion. This provides an excellent example of how the transport mechanism affects membrane selectivity. Helium is the molecule with higher permeability, but the He/N_2 and He/Ar flux ratios decreased by more than 10% in relation to Knudsen transport alone, due to the intrusion of viscous flow. Another membrane, with smaller pores, would show no viscous flow and therefore maximize selectivity.

Finally, the experiment illustrates an effective method for measuring the membrane average pore size.

A possible improvement to this setup would allow for the mean pressure in the module to be set in a range above or below atmospheric pressure. It can be seen from Eq. (4) that, say, for a constant pressure drop across the membrane at higher mean pressures, the transport becomes predominantly Poiseuille flow. This would imply adding a pressure sensor, a valve, and a vacuum pump at the module's outlet stream.

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NOMENCLATURE

D_k	$\frac{2}{3} r_p \sqrt{\frac{8\,RT}{\pi M}}$ Knudsen diffusivity ($m^2\ s^{-1}$)
D_v	$\frac{P_\ell r_p^2}{16\,\mu}\left(m^2\ s^{-1}\right)$
F	volumetric flow ($m^3\ s^{-1}$)
ℓ	membrane thickness (m)
L	permeability ($m^3\ s^{-1} N^{-1}\ m^2$)
M	molecular weight ($g\ mol^{-1}$)
N	molar flux ($mol\ m^{-2}\ s^{-1}$)
N_k	molar flux due to Knudsen diffusion ($mol\ m^{-2}\ s^{-1}$)
N_v	molar flux due to viscous flow ($mol\ m^{-2}\ s^{-1}$)
P_h	inlet pressure ($N\ m^{-2}$)
P_ℓ	outlet pressure ($N\ m^{-2}$)
r_p	membrane average pore radius (m)
R	ideal gas constant (8.314 $J\ K^{-1}\ mol^{-1}$)
T	temperature (K)
v_k	$\frac{2}{3}\sqrt{\frac{8\,RT}{\pi M}}$
ε	membrane porosity
μ	gas viscosity ($Kg\ m^{-1}\ s^{-1}$)
τ	membrane tortuosity

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