# 1)
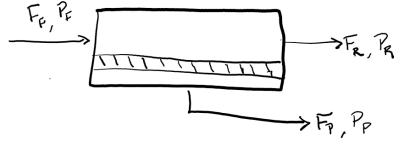


$T = 30\ °C$

$F_F = 1000\ \text{kmol/hr}$

$P_F = 5500\ \text{kPa}$

$y_{F,N} = 0.2$

$F_P = 1000\ \text{kmol/hr}$

$P_P = 100\ \text{kPa}$

$F_{P,M} = 180\ \text{kmol/hr}$

$F_{R,N} = 20\ \text{kmol/hr}$

$P_R = 5450\ \text{kmol/hr}$

$\bar{P}_{M_N} = 50000\ \text{barrer/cm}$

$\bar{P}_{M_M} = 10000\ \text{barrer/cm}$

**Assume:** $N = N_2$, $M = CH_4$

**Solve:**

**a.**

An overall material balance around the membrane gives the following table.

**Table 1:** $N_2$-$CH_4$ Membrane Separation Material Balance

| Comp. | $F_{F,i}$ (kmol/h) | $y_{F,i}$ | $F_{P,i}$ (kmol/h) | $y_{P,i}$ | $F_{R,i}$ (kmol/h) | $y_{R,i}$ |
|---|---|---|---|---|---|---|
| $N_2$ | 200 | 0.20 | 180 | 0.50 | 20 | 0.03 |
| $CH_4$ | 800 | 0.80 | 180 | 0.50 | 620 | 0.97 |
| $\Sigma$ | 1000 | 1.00 | 360 | 1.00 | 640 | 1.00 |

By applying a Fick model to the membrane, we have,

$$N_N = \bar{P}_{M_N}\Delta P_N,$$

or by integrating over the membrane area, assuming all quantities are constant over the area,

$$F_{P,N} = \bar{P}_{M_N}\Delta P_N A.$$

Thus,

$$A = \frac{F_{P,N}}{\bar{P}_{M_N}\Delta P_N}.$$

The average driving pressure is given by,

$$\begin{aligned}
\Delta P_N &= \frac{P_F y_{F,N} + P_R y_{R,N}}{2} - P_{P,N} \\
&= \left[\frac{(5500)(0.20) + (5450)(0.03)}{2} - 100(0.50)\right]\ \text{kPa} \\
&= 585\ \text{kPa}.
\end{aligned}$$

Unit conversions...

$$\bar{P}_{M_N} = \left(5000000\ \frac{\text{barrer}}{\text{m}}\right)\left(\frac{3.348 \times 10^{-19}\ \text{kmol} \cdot \text{m}}{\text{barrer} \cdot \text{m}^2 \cdot \text{s} \cdot \text{Pa}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right) = 6.03 \times 10^{-9}\frac{(\text{kmol/h})}{\text{m}^2 \cdot \text{Pa}}.$$

This gives,

$$A = \frac{180 \text{ (kmol/h)}}{(585156 \text{ Pa}) \left(6.03 \times 10^{-9} \dfrac{\text{kmol/h}}{\text{m}^2 \cdot \text{Pa}}\right)} = 51044 \text{ m}^2.$$

Performing the same calculation using the methane partial pressures gives $A = 31180 \text{ m}^2$. This inconsistency is likely due to errors in the permeance values which are amplified when dividing to get the area. We will take the largest area to ensure the specified flow rate is achieved.

## b.

In gas separations, the pore size must be small to achieve a good separation, thus, the main mode of transport is diffusion across the membrane. Since the pressure difference is high, Knudsen diffusion is not as significant and the effective diffusivity may be approximated by the corrected molecular diffusivity, $\varepsilon D_i / \tau$. Furthermore, the temperature dependence of the molecular diffusivity is proportional to $T^{1.75}$ [1]. Assuming the pressure difference is kept constant, the flux of a species, $i$, is then estimated by,

$$N_i \sim \text{const.} * \frac{\varepsilon T^{1.75}}{\tau \ell R T} \Delta P_i \sim \text{const.} * T^{0.75}.$$

Thus, the flux is proportional to $T^{0.75}$ and an increase in temperature will cause a sizable increase in the flux. This is physically reasonable, at higher temperatures, we expect a higher diffusion rate. However, if we take the ratio of any two fluxes, we find,

$$\frac{N_i}{N_j} \sim \text{const.} * \frac{\Delta P_i}{\Delta P_j},$$

where the temperature dependence has dropped out since the permeance values have approximately the same temperature dependence. This means that the degree of separation (flux ratio) is fixed by the driving forces (thermodynamics) and temperature only acts to change the rate (transport) of the process.

## c.

To maximize the flux, we would need a larger void fraction, $\varepsilon$, a low tortuosity, $\tau$, and a small membrane thickness, $\ell$. Since the pressure difference is high, it will likely be hard to make $\ell$ small. If $\varepsilon$ is too large, then it is unlikely a good separation will occur since nearly everything would be allowed to pass, effectively giving bulk flow. This leaves $\tau$ to be minimized in order to minimize the resistance to flow. Additionally, the pore area to membrane volume ratio, $a_v$, is important, which is also related to the pore diameter and how restricted the diffusion is.

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[1]Seader, J.D., Henley, E.J., Roper, D.K., *Separation Process Principles with Applications Using Process Simulators*, John Wiley & Sons, Inc., 2016.

## 2)
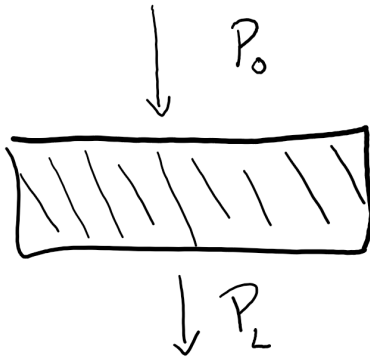


$$T = 70 \ ^\circ\text{C}$$
$$\varepsilon = 0.32$$
$$d_p = 0.30 \times 10^{-6} \text{ m}$$
$$\tau = 1.8$$
$$P_0 = 500 \text{ kPa}$$
$$P_L = 125 \text{ kPa}$$
$$\ell = 1.0 \times 10^{-6} \text{ m}$$

**Assume:**

**Solve:**

Since there is a high pressure difference between the streams, a bulk flow model may be used,

$$\frac{N_W}{\rho} = N = \frac{\varepsilon d_p^2}{32\tau\mu\ell}\Delta P.$$

With $\mu = 0.4005 \times 10^{-3}$ Pa $\cdot$ s [2],

$$N = \frac{(0.32)(0.30^2 \times 10^{-12} \text{ m}^2)(375000 \text{ Pa})}{32(1.8)(0.4005 \times 10^{-3} \text{ Pa} \cdot \text{s})(1.0 \times 10^{-6} \text{ m})}\left(\frac{24 \times 3600 \text{ s}}{1 \text{ day}}\right),$$

giving,

$$\boxed{N = 40452 \text{ m}^3/(\text{m}^2 \cdot \text{day})}.$$

Given a 5 % uncertainty [3] in $(\tau, d_p, \varepsilon, \ell)$, we may take $(\tau, d_p, \varepsilon, \ell)_\mu = (1.8, 0.3 \ \mu\text{m}, 0.32, 1 \ \mu\text{m})$ as mean values and approximate the error by Gaussian noise with mean 0 and standard deviation, $2\sigma = 0.05(\tau, d_p, \varepsilon, \ell)_\mu$. This means about 95 % of the generated input data will lie within the 5 % uncertainty bound. Using these Gaussian random variables, we may simulate many observations and generate a histogram of the resulting flux distribution. This was done in Python which yields the following plot of the density function where the area under the histogram is 1.

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[2]Incropera, F. P., Bergman, T. L., Lavine, A. S., Dewitt, D. P., *Fundamentals of Heat and Mass Transfer*, 7th ed., Wiley, 2013

[3]If we take the 5 % error as strict bound, then the max flux is $N = 51888$ m$^3$/(m$^2 \cdot$ day) and the minimum flux is $N = 31458$ m$^3$/(m$^2 \cdot$ day).
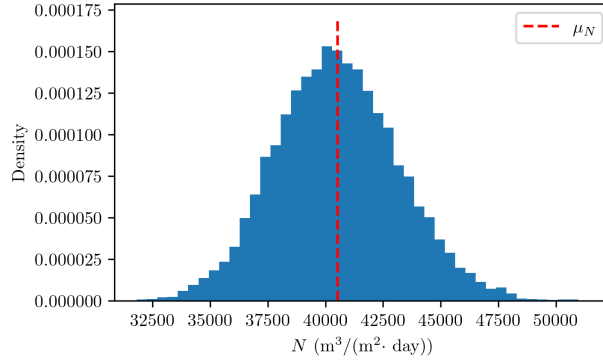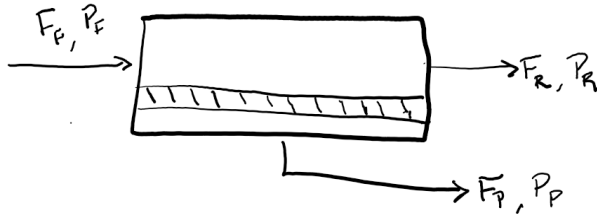
Figure 1: Histogram for the simulation of 10000 flux values from random $(\tau, d_p, \varepsilon, \ell)$ data

From this, we see that the uncertainty causes about a $\pm 7000 \ \mathrm{m^3/(m^2 \cdot day)}$ deviation from the mean ($\sim 17$ %) with some outliers. However, most of the mass of the distribution lies in a bell shape around the mean value of $N = 40452 \ \mathrm{m^3/(m^2 \cdot day)}$.

## 3)



$d_p = 40 \times 10^{-8} \ \mathrm{cm}$

$\Delta P \sim 105 \ \mathrm{psia}$

$P_{M_{He}} = 117000 \ \mathrm{barrer}$

$P_{M_{CO2}} = 68000 \ \mathrm{barrer}$

**Assume:** Knudsen flow

**Solve:**

For the flow of gasses through a porous membrane, the permeability can be modeled by,

$$P_{M_i} = \frac{\varepsilon}{RT\tau} \left[ \frac{1}{(1/D_i) + (1/D_{K_i})} \right].$$

In the limit of pure Knudsen diffusion,

$$P_{M_i} = \frac{\varepsilon}{RT\tau} D_{K_i}.$$

$D_{K_i}$ is further modeled by,

$$D_{K_i} = 4850 \, d_p (T/M_i)^{1/2},$$

where $[D_{K_i}] = \mathrm{cm^2/s}$, $[d_p] = \mathrm{cm}$, $[T] = \mathrm{K}$, and $[M_i] = \mathrm{kg/kmol}$. Assuming that the helium and carbon dioxide are both in Knudsen flow and operating under the same conditions and membrane, then the ratio of permeabilities is,

$$\frac{P_{M_{CO2}}}{P_{M_{He}}} = \left( \frac{M_{He}}{M_{CO2}} \right)^{1/2}.$$

Thus,

$$P_{M_{CO2}} = (117000 \text{ barrer}) \left( \frac{4.002 \text{ g/mol}}{44.01 \text{ g/mol}} \right)^{1/2} = 35282 \text{ barrer}.$$

This is 48 % less than the experimental value of $P_{M_{CO2}}$. This large error is likely because pure Knudsen flow does not apply to the carbon dioxide case. However, if we still assume Knudsen flow for the helium, but not for the carbon dioxide, then,

$$\frac{P_{M_{CO2}}}{P_{M_{He}}} = \frac{1}{D_{K_{He}}} \frac{1}{(1/D_{CO2}) + (1/D_{K_{CO2}})}$$
$$= \frac{1}{\left( \frac{M_{CO2}}{M_{He}} \right)^{1/2} + \frac{D_{K_{He}}}{D_{K_{CO2}}}}.$$

To get a rough estimate of this correction, the binary diffusivity of carbon dioxide in air is $0.177 \text{ cm}^2/\text{s}$ at 317.2 K [4], using this, we may calculate the new permeability at the same temperature to be $P_{M_{CO2}} = 33778$ barrer ... which is an even worse estimate. Another possibility is that helium is a much smaller molecule and the flow is less restricted compared to carbon dioxide, but I think that would still decrease the predicted permeability. The last possibility is just that Knudsen flow is not a good model for passing $CO_2$ through the given membrane.

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[4]Seader, J.D., Henley, E.J., Roper, K.D., *Separation Process Principles with Applications Using Process Simulators*, John Wiley & Sons, Inc., 2016.