Asymptotic Analysis of Gas Separation by a Membrane Module

Osman A. Basaran, Steven R. Auvil
Air Products & Chemicals, Inc.
Allentown, PA 18105

The nonlinear ordinary differential equations that govern the performance of membrane modules for gas separations are well known. These equations have been solved numerically by many investigators (e.g., Hwang and Kammermeyer, 1975; Antonson et al., 1977; Chern et al. 1985; Pan, 1986). Boucif et al. (1984, 1986) have obtained approximate solutions to the governing equations as series in powers of dimensionless membrane area. Their methodology reduces the original set of differential equations to one or more nonlinear algebraic equations that, however, must still be solved numerically. What has been lacking in the literature is an analysis by asymptotic methods that provides valuable insight into the performance of membrane modules in certain limiting regimes of their operation.

By way of example, the equations that govern the performance of membrane modules are solved in this paper by asymptotic methods for the case of a binary gas mixture in a cross-flow module. The starting point of this analysis is identifying a parameter in the governing equations that is either small or large. Perturbation expansions are then formed in terms of the small or the reciprocal of the large parameter. The analysis that is carried out is similar in principle to the well-known analyses of the Navier-Stokes equations at low and high Reynolds numbers (Van Dyke, 1975).

The limits as $\alpha \rightarrow 1$ and $\alpha \rightarrow \infty$, where α is the selectivity of the fast-permeating gas with respect to the slow-permeating gas, are identified as the two asymptotic regimes. Membranes that have a selectivity of order 1 or much greater than 1 abound in practice. Many polymeric membranes fall into the former class. By way of example, methane to nitrogen selectivity is about 3.4 in silicone rubber (Robb, 1968). Most facilitated transport membranes are examples from the latter class (e.g., Kemena et al., 1983).

Governing Equations, Initial Conditions, and Asymptotic Regimes

The total molar flow rate, q, and the mole fraction of the fast permeating gas, x, of a binary gas mixture on the feed side of the membrane in the module shown in Figure 1 are governed by one-dimensional, depth-averaged mass balance equations (e.g., Hwang and Kammermeyer, 1975):

$$\frac{dq}{da} = -[1 - p_r + (\alpha - 1)(x - p_r y)], \tag{1}$$

$$\frac{dx}{da} = -\frac{1}{q}[\alpha(x - p_r y) + x\frac{dq}{da}]. \tag{2}$$

In Eqs. 1 and 2 and throughout this paper, it is assumed that the pressure drops on the feed and permeate sides are negligible; the relative importance of convective mass transport is large compared to diffusive mass transport in the direction parallel to the membrane surface on the feed side; and conditions of plug-flow and plug-like concentration profiles exist on the feed side of the membrane. These are usually excellent approximations in practice. Equations 1 and 2 are already dimensionless. Here q is measured in units of Q_{in}, the total molar flow rate on the feed side at the entrance to the module. The selectivity α and the pressure ratio p_r are both constants and are defined as

$$\alpha \equiv P_i/P_j, \quad p_r \equiv p_p/p_f, \tag{3}$$

where P_i is the permeability of the fast gas and P_j that of the slow gas and p_p is the total pressure on the permeate side and p_f that on the feed side. The ranges of the parameters in Eq. 3 are $1 \leq \alpha < \infty$ and $0 \leq p_r \leq 1$. The dimensionless area, a, and its dimensional counterpart, A, are related by

$$a \equiv BA/A_c, \quad B \equiv \frac{p_f P_j/L}{Q_{in}/A_c}. \tag{4}$$

In Eq. 4, A_c is a characteristic area to be defined shortly, L is the membrane thickness, and B is a dimensionless group that measures the relative importance of the molar flux permeating across the membrane to the convective molar flux entering the module.

Correspondence concerning this paper should be addressed to Osman A. Basaran who is presently with Oak Ridge National Laboratory, Oak Ridge, TN 37831.

For modules based on asymmetric membranes and ones of the spiral-wound type, the flow pattern is well approximated as cross flow (Pan, 1983, 1986). The mole fractions on the permeate side are then governed by mass balances that reduce to nonlinear algebraic equations (e.g., Hwang and Kammermeyer, 1975). For a binary mixture, an exact solution by means of the quadratic formula yields the following expression for the mole fraction of the fast gas on the permeate side:

$$y = \frac{1 + (x + p_r)(\alpha - 1) - \sqrt{[1 + (x + p_r)(\alpha - 1)]^2 - 4\alpha(\alpha - 1)\, x p_r}}{2p_r(\alpha - 1)}. \tag{5}$$

However, the analysis reported in this paper is not just restricted to cross-flow modules, but is easily generalized to cocurrent-flow and counter-current-flow modules.

Governing Eqs. 1, 2, and 5 are solved subject to the initial conditions

$$q(0) = 1, \quad x(0) = x_{in}, \tag{6}$$

where x_{in} is the mole fraction of the fast gas on the feed side at the entrance to the module.

Two situations often arise in practice:

1 The total membrane area A_T is specified *a priori*. In this case, $A_c = A_T$ and the governing equations are integrated until $a = B$.

2 The desired mole fraction of the fast (or slow) gas on the feed side at the exit from the module, i.e., in the reject stream, x_{out} (or $1 - x_{out}$) is specified *a priori*. In this case, $A_c = Q_{in}/(p_f P_j / L)$ and $B = 1$ and the governing equations are integrated until $x = x_{out}$.

When the permeabilities of the two gases are equal, $\alpha = 1$ and Eqs. 1, 2, and 5 have the simple solution

$$q = 1 - (1 - p_r)a, \quad x = y = x_{in}. \tag{7}$$

Thus, the situation in which the permeabilities of the two gases are not too different should be analyzable by forming regular perturbation expansions of the unknowns q, x, and y about the base state at Eq. 7 in powers of the small parameter $\alpha - 1$.

When the permeability of the fast gas is infinitely large compared to that of the slow gas, $\alpha \rightarrow \infty$ and Eqs. 1 and 2 have the solution

$$x = p_r y, \tag{8}$$

and Eq. 5 has the solution

$$y = \frac{1}{2p_r}(x + p_r - |x - p_r|). \tag{9}$$

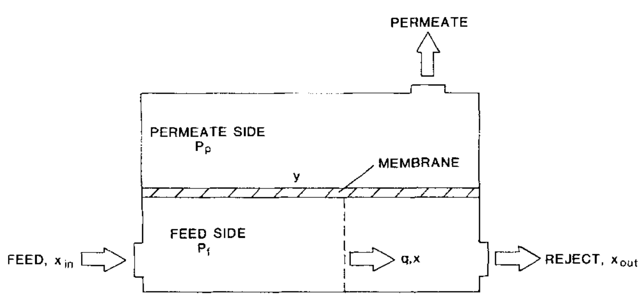

Figure 1. Schematic of a membrane module.

Equations 8 and 9 have two distinct solutions. When $x, x_{in} \leq p_r$

$$y = x/p_r, \tag{10}$$

and when $x, x_{in} > p_r$,

$$x = p_r, \quad y = 1. \tag{11}$$

The solution for the mole fraction of the fast gas on the feed side at Eq. 11 does not satisfy the initial condition at Eq. 6. This suggests that a boundary layer is present near the entrance to the module. Inside this boundary layer, x decays rapidly from x_{in} to p_r. Figure 2 is a qualitative sketch of the solutions at Eqs. 10 and 11.

Physically, what is happening is as follows. The flux, N, of the fast gas across the membrane at any point in the module is $N = \alpha(x - p_r y)$ (see Eqs. 1 and 2). As $\alpha \rightarrow \infty$, the only way that the flux N can remain finite is for the driving force $x - p_r y \rightarrow 0$. Because $0 \leq y \leq 1$, whether $x_{in} \leq p_r$ or $x_{in} > p_r$ then determines which of the two solutions at Eqs. 10 and 11 applies.

The difference between the two cases depicted in Figure 2 is

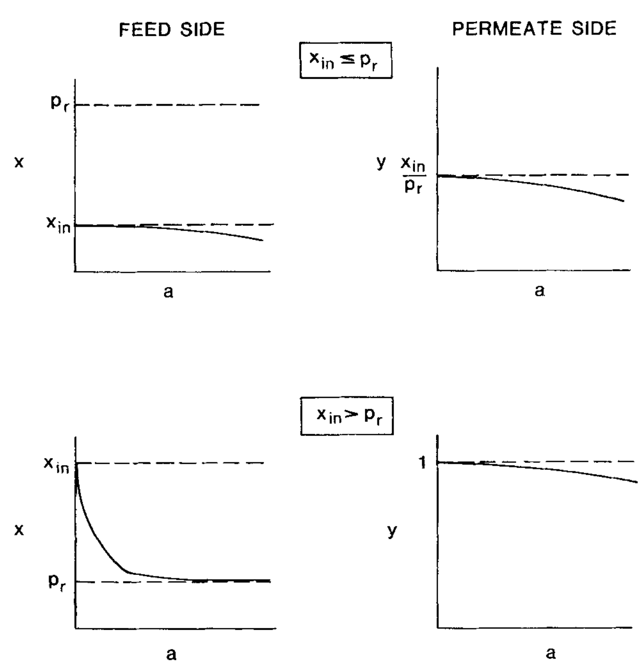

Figure 2. Qualitative variation of the mole fractions x and y with position along the module in the limit $\alpha \rightarrow \infty$.

clarified further by a simple calculation. If $\alpha = 10^3$, $x_{in} = 0.1$, and $p_r = 0.5$, Eqs. 1, 2, and 5 when evaluated at the entrance to the module, i.e., at $a = 0$, give

$$y \approx 0.2, \quad dq/da \approx -0.6, \quad dx/da \approx -0.06. \tag{12}$$

By contrast, if $\alpha = 10^3$, $x_{in} = 0.5$, and $p_r = 0.1$, Eqs. 1, 2, and 5 when evaluated at $a = 0$ yield

$$y \approx 1, \quad dq/da \approx -401, \quad dx/da \approx -200. \tag{13}$$

The situation in which the permeability of one gas is much larger than that of the other gas should therefore be analyzable by asymptotic analysis in terms of the small parameter α^{-1}. The case $x_{in} \leq p_r$ is solvable by regular perturbation analysis; the case $x_{in} > p_r$ requires a singular perturbation analysis.

Case of Nearly Equal Permeabilities: $\alpha \longrightarrow 1$

Solutions of Eqs. 1, 2, and 5 are sought by expanding the unknowns q, x, and y in powers of the small parameter $\epsilon \equiv \alpha - 1 \ll 1$:

$$q = q_0 + \epsilon q_1 + \cdots, \quad x = x_0 + \epsilon x_1 + \cdots, \quad y = y_0 + \epsilon y_1 + \ldots, \tag{14}$$

where the zeroth-order solutions q_0, x_0, and y_0 are given by Eq. 7.

The first-order corrections to the molar-flow-rate and the mole fractions are:

$$q_1 = -x_{in}(1 - p_r)a, \tag{15}$$

$$x_1 = x_{in}(1 - x_{in})(1 - p_r)\log[1 - (1 - p_r)a], \tag{16}$$

$$y_1 = x_{in}(1 - x_{in})(1 - p_r)\{1 + \log[1 - (1 - p_r)a]\}. \tag{17}$$

Eqs. 16 and 17 show that $y_1 \geq x_1$ and hence, $y \geq x$ to $0(\epsilon)$ at each point along the module. This is in accord with physical intuition because the membrane is selectively separating the fast gas from the slow gas.

The second-order corrections to the unknowns are

$$q_2 = x_{in}(1 - x_{in})(1 - p_r) \cdot \{a + [1 - (1 - p_r)a]\log[1 - (1 - p_r)a]\}, \tag{18}$$

$$x_2 = x_{in}(1 - x_{in})(1 - p_r)\Big\{-[x_{in} + p_r(1 - 2x_{in})] \cdot \log[1 - (1 - p_r)a] - \frac{x_{in}(1 - p_r)a}{[1 - (1 - p_r)a]} + \frac{1}{2}(1 - 2x_{in})(1 - p_r)\log^2[1 - (1 - p_r)a]\Big\} \tag{19}$$

$$y_2 = x_{in}(1 - x_{in})(1 - p_r)\left[-\frac{x_{in}(1 - p_r)a}{[1 - (1 - p_r)a]} - [x_{in} + p_r \cdot (1 - 2x_{in})]\{1 + \log[1 - (1 - p_r)a]\} + (1 - 2x_{in})(1 - p_r) \cdot \log[1 - (1 - p_r)a]\left\{1 + \frac{1}{2}\log[1 - (1 - p_r)a]\right\}\right]. \tag{20}$$

Case of Very Different Permeabilities: $\alpha \longrightarrow \infty$

The small perturbation parameter is now defined as $\epsilon \equiv \alpha^{-1} \ll 1$.

Situation in which $x_{in} \leq p_r$

Solutions of Eqs. 1, 2, and 5 are sought once more by expanding the unknowns as in Eq. 14. At zeroth order, Eqs. 1, 2, and 5 all yield:

$$x_0 = p_r y_0. \tag{21}$$

Solution of the first-order problem then gives:

$$q_0(1 - x_0) - (1 - x_{in}) = -(1 - p_r)a \tag{22}$$

$$q_0 = \left(\frac{x_0}{x_{in}}\right)^{p_r/(1 - p_r)}. \tag{23}$$

Equation 23 can be substituted into Eq. 22 to yield an equation that governs how x_0 varies with position along the module.

Situation in which $x_{in} > p_r$

In the limit as $\alpha \rightarrow \infty$, the solution to Eqs. 1, 2, and 5 to the highest order are given by Eq. 11. The solution for the mole fraction of the fast gas on the feed side does not satisfy the initial condition at Eq. 6 and is thus an outer solution to Eqs. 1, 2, and 5—$x_{outer} = p_r$. Therefore, near the entrance to the module, i.e., $a = 0$, the membrane area is mathematically stretched by means of the transformation $\mathcal{A} \equiv a/\epsilon$ (e.g., Lin and Segel, 1974). With this area stretch, the solution of Eqs. 1 and 2 to the highest order are:

$$Q(1 - X) = 1 - x_{in} = \text{constant}, \tag{24}$$

$$\frac{1}{1 - p_r}\left[\frac{X - x_{in}}{(1 - X)(1 - x_{in})} + \frac{1}{1 - p_r} \cdot \log\left(\frac{X - p_r}{x_{in} - p_r} \cdot \frac{1 - x_{in}}{1 - X}\right)\right] = -\frac{\mathcal{A}}{1 - x_{in}}. \tag{25}$$

In Eqs. 24 and 25 X and Q denote the boundary layer or inner solutions to the mole fraction of the fast gas and the total molar flow rate on the feed side. In arriving at Eqs. 24 and 25, use is made of the fact $Y = 1$, where Y is the boundary layer solution to the mole fraction of the fast gas on the permeate side. It is easy to show from Eq. 25 that

$$\lim_{\mathcal{A} \to \infty} X = p_r = x_{outer}. \tag{26}$$

Thus the matching of the inner and outer solutions is assured. Furthermore, it follows from Eqs. 24 and 25 that

$$\lim_{\mathcal{A} \to \infty} Q = \frac{1 - x_{in}}{1 - p_r} \tag{27}$$

Comparison of the Predictions of Asymptotic and Numerical Analyses

In what follows, subscript E denotes the "exact" solution of Eqs. 1, 2, and 5 obtained by numerical integration of these equations.

In Figure 3, the predictions of the asymptotic analysis for $\alpha \rightarrow 1$ are compared to those of numerically solving Eqs. 1, 2, and 5 for situations in which $x_{in} = 0.1$, $p_r = 0.1$, and $\alpha = 1.2$ or 2. The equations were integrated until $x_{out} = 0.05$. In Figure 3, $x^{(2)} \equiv x_0 + \epsilon x_1 + \epsilon^2 x_2$. Figure 3 shows that the agreement between the exact and the approximate solutions is excellent when $\alpha - 1$ (=0.2) is small and that it is very good even when $\alpha - 1$ (=1) is no longer small and is in fact a 0(1) quantity.

In Figure 4, the predictions of the asymptotic analysis for $\alpha \rightarrow \infty$ when $x_{in} \le p_r$ are compared to those of numerically solving Eqs. 1, 2, and 5 for the situation in which $\alpha = 100$, $x_{in} = 0.1$, and $p_r = 0.5$. The equations were integrated until $x_{out} = 0.05$. Excellent agreement is found between the asymptotic and the exact solutions. Note that the ratio $y/x = 2 = 1/p_r$ everywhere in the module, as predicted by Eq. 21. The total dimensionless area calculated by the asymptotic analysis is 0.854 and that by the numerical solution 0.87.

In Figure 5, the predictions of the asymptotic analysis for $\alpha \rightarrow \infty$ when $x_{in} > p_r$ are compared to those of numerically solving Eqs. 1, 2, and 5 for the situation in which $\alpha = 1{,}000$, $x_{in} = 0.5$, and $p_r = 0.1$. The equations were integrated until $x_{out} = 0.105$. Figure 5 makes plain the singular behavior of Eqs. 1 and 2 for this set of parameter values. The uniformly valid solutions q_0 and x_0, given by Eqs. 24 and 25, respectively, decay in the manner alluded to in Figure 2. As $\mathcal{A} \rightarrow \infty$, it follows from Eqs. 26 and 27 that

$$\lim_{\mathcal{A}\rightarrow\infty} X = 0.1, \quad \lim_{\mathcal{A}\rightarrow\infty} Q = 0.556. \tag{28}$$

It is then natural to ask if values of $x_{out} < p_r$ can ever be realized when $\alpha \gg 1$ and $x_{in} > p_r$. Figure 6 shows how the dimensionless total membrane area as predicted by numerically solving the governing equations varies as a function of the mole fraction of the fast gas at the exit from the module under the same conditions as in Figure 5. The membrane area grows exponentially once the mole fraction of the fast gas in the reject stream falls below $p_r = 0.1$.

Figure 5 also shows that the mole fraction of the fast gas on the permeate side varies by only 7% from its initial value of one as the length of the whole module is traversed.

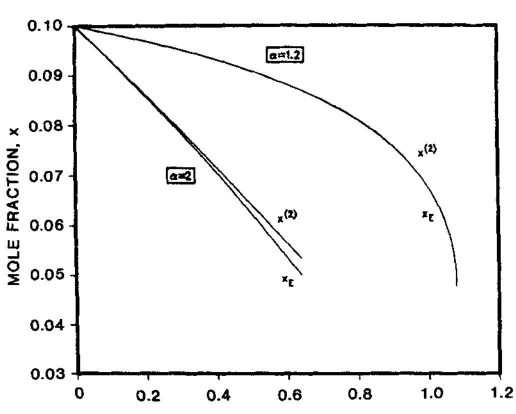

Figure 3. Mole fraction of the fast gas on the feed side of the membrane versus position in the module.
$x_{in} = 0.1, p_r = 0.1$

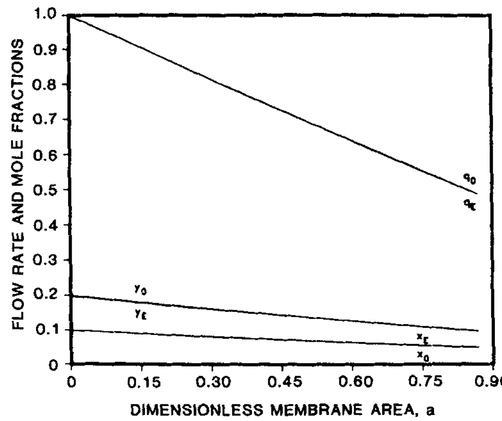

Figure 4. Molar-flow-rate and mole fraction of the fast gas on the feed and permeate sides of the membrane vs. position in the module.
$\alpha = 100, x_{in} = 0.1, p_r = 0.5$

Figure 7 shows how the dimensionless total membrane area varies with the selectivity for a situation in which $x_{in} < p_r$. The membrane area shown is that required to reduce the mole fraction of the fast gas in the feed from 0.2 to 0.1. In both Figures 7 and 8, the curves labeled "exact area" are the areas that result from integrating Eqs. 1, 2 and 5 numerically; the curves labeled "$\alpha - 1 \ll 1$ asymptotics" are the areas predicted by asymptotic analysis.

In Figure 7, the curve labeled "$\alpha \gg 1$ asymptotics" is the area predicted by Eq. 22. Figure 7 shows that the $\alpha - 1 \ll 1$ asymptotics breaks down under the conditions shown when the selectivity exceeds 3. Increasing the radius of convergence of the asymptotic solution requires extending the perturbation series for $x = x_0 + \epsilon x_1 + \cdots$ to higher orders than second order by delegating the rapidly mounting algebraic labor to a computer (Van Dyke, 1984). The numerical calculations and the $\alpha \gg 1$ asymptotics show that a finite membrane area is required even if the selectivity was infinitely large. Figure 7 shows that the membrane area asymptotically approaches 0.188 as $\alpha \rightarrow \infty$.

Figure 8 shows how the dimensionless membrane area varies

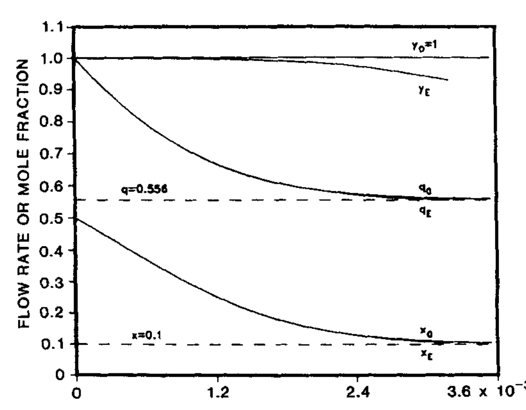

Figure 5. Molar-flow-rate and mole fraction of the fast gas on the feed and permeate sides of the membrane versus position in the module.
$\alpha = 1{,}000, x_{in} = 0.5, p_r = 0.1$

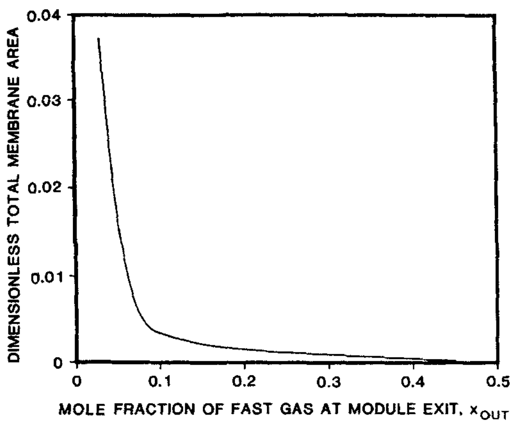

Figure 6. Total membrane area as a function of mole fraction of fast gas at module exit.
$x_{in} = 0.5, p_r = 0.1, \alpha = 1{,}000$

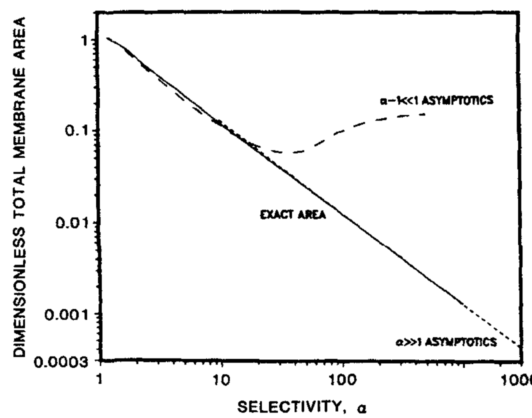

Figure 8. Total membrane area as a function of selectivity.
$x_{in} = 0.4, x_{out} = 0.2, p_r = 0.1$

with the selectivity for a situation in which $x_{in} > p_r$. The membrane area shown is that required to reduce the mole fraction of the fast gas in the feed from 0.4 to 0.2. In Figure 8, the curve labeled "$\alpha \gg 1$ asymptotics" is the area predicted by Eq. 25 referred to earlier. Under the conditions of Figure 8, the $\alpha - 1 \ll$ asymptotics are valid until the selectivity exceeds about 20. The curves labeled "exact area" and "$\alpha \gg 1$ asymptotics" are in agreement to within 1% for selectivities exceeding ten. In this case, the numerical calculations and the $\alpha \gg 1$ asymptotics show that the membrane area required to affect a separation approaches zero as the selectivity approaches infinity. This is physically plausible because the separation occurs inside a thin-boundary-layer at the entrance to the module. For the conditions used in Figure 8, the asymptotic and the numerical results are in excellent agreement over the whole range of selectivities $1 \leq \alpha < \infty$.

Conclusions

The asymptotic formulas reported in this work can be used to gain a good understanding of membrane performance without resorting to extensive numerical calculations. In fact, the formulas obtained are simple enough in form to make them suitable for "back-of-the-envelope" calculations. The asymptotic expressions for the total molar-flow-rate can be used in approximately sizing and costing the compressors in a cycle where a cascade of membranes is used. The asymptotic expressions for the mole fractions (as functions of area) can be used for rapidly estimating the membrane area and the membrane cost required to affect a desired separation.

Figures 7 and 8, and similar figures, can be extremely valuable in obtaining quick estimates of membrane areas required to affect a desired separation. Figure 7 teaches that no matter how large the selectivity becomes, a finite membrane area will be needed to achieve the desired separation whenever $x_{in} \leq p_r$. Figures 6 and 8 teach that when the selectivity is large and $x_{in} > p_r$, little membrane area will be required if $x_{out} \geq p_r$. However, the membrane area becomes prohibitively large if $x_{out} \ll p_r$, Figure 6.

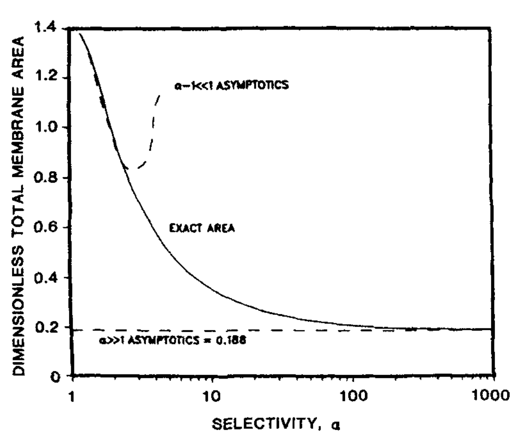

Figure 7. Total membrane area as a function of selectivity.
$x_{in} = 0.2, x_{out} = 0.1, p_r = 0.3$

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Notation

a, A = dimensionless and dimensional membrane areas
$\mathcal{A} \equiv a/\epsilon$ = boundary layer independent variable, or stretched area, dimensionless
A_c = characteristic (dimensional) area defined in the text
A_T = dimensional total membrane area
$B \equiv p_f P_j / L / (Q_{in}/A_c)$ = dimensionless group that measures the relative importance of permeation to convection
L = membrane thickness
N = dimensionless flux of the fast gas across the membrane
Q_{in} = dimensional total molar flow rate on the feed side at the entrance to the module
Q, X, Y = boundary-layer-solutions for q, x, and y, dimensionless
p_f, p_p = total pressure on the feed and permeate sides
$p_r \equiv p_p/p_f$ = permeate to feed pressure ratio, dimensionless

P_i, P_j = permeabilities of the fast and slow gases
q = dimensionless total molar-flow-rate on the feed side
$q_i, i = 1, \ldots$ = ith order correction to the dimensionless total molar-flow-rate on the feed side
x, y = mole fraction of the fast permeating gas on the feed and permeate sides
$x^{(i)}, i = 1, \ldots$ = ith order solution to the mole fraction of the fast gas on the feed side
$x_i, y_i, i = 1, \ldots$ = ith order correction to the mole fraction of the fast gas on the feed and permeate sides
x_{in}, x_{out} = mole fraction of the fast permeating gas on the feed side at the inlet and the outlet to the module

Greek letters

$\alpha = P_i/P_j$ = selectivity or ratio of permeability of fast gas to that of slow gas, dimensionless
$\epsilon = \alpha - 1$ or α^{-1} = perturbation parameter, dimensionless

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