Modeling of Permeators with Two Different Types of Polymer Membranes

Mathematical models have been developed for the separation of binary gas mixtures in permeator modules housing two different types of membranes simultaneously. The membranes are selected so as to exhibit reverse selectivities toward the components of a mixture, i.e., so that one membrane is more permeable to one of the components while the second membrane is more permeable to the other component. The mathematical models describe the membrane separation process for three kinds of flow patterns of the permeated (low pressure) and unpermeated (high pressure) gas streams in the permeator, namely, "perfect mixing," countercurrent flow, and cocurrent flow. Numerical solutions of the models indicate that the extent of separation achievable in a two-membrane permeator can be much higher than in a conventional single-membrane permeator. Also, for given product compositions, the membrane area requirements of the former permeator can be lower than those of the latter. Countercurrent flow is generally the most efficient flow pattern in a two-membrane permeator, and "perfect mixing" is the least efficient one, but the opposite is true under special operating conditions.

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SCOPE

The separation of gas mixtures by selective permeation through polymer membranes is currently under active investigation by many laboratories due to the fact that this separation technique is potentially energy-efficient. Additionally, the required process equipment is simple, modular, and relatively easy to control.

Significant advances have been made in membrane technology for gas separation in recent years. These advances may be placed into two categories: membrane materials and process design concepts. The most noteworthy advance in materials has been the development of asymmetric hollow fiber and composite membranes that exhibit high gas permeabilities as well as high selectivities for specific components of gas mixtures. In the area of process design, one of the most interesting innovations has been the simultaneous use of two or more different types of membranes for a given separation process (Ohno et al., 1973–78; Kimura et al., 1973). The membranes are chosen so as to exhibit special selectivities for different components of a gas mixture to be separated. Thus, according to this concept, a binary gas mixture is best separated by means of two different membranes, one of which is more permeable to one of the components of the mixture while the other membrane is more permeable to the second component.

The advantages of using two or more different types of membranes for a given separation process, rather than a single type of membrane, are twofold: The extent of separation is increased, and the extent of recovery of a desired component of the feed mixture is also increased. The use of more than one type of membrane, where possible, should therefore lower the energy and capital investment costs of membrane separation processes. An additional advantage of multimembrane systems lies in their ability to produce more than two product streams. Hence, such systems are potentially useful for the separation of multicomponent gas mixtures.

When the multimembrane concept is reduced to practice, the different types of membranes employed can be housed in the same permeator module, or vessel. Alternatively, each type of membrane can be housed in a different permeator, and these permeators can then be connected either in series or parallel. A recent study (Stern et al., 1983) has shown that the most effective way of separating binary mixtures with two different types of membranes is to enclose both types of membranes in the same permeator. It is possible that the same result will be obtained for membrane separation processes in which more than two types of membranes are used, but no studies of such processes have been published.

The objective of the present study was to develop mathematical models that describe the separation of binary gas mixtures by selective permeation through two different types of membranes housed in the same permeator module. As mentioned above, the membranes must exhibit reverse selectivities for the components of the mixtures. The models consider three different flow patterns of the permeated (low pressure) and unpermeated (high pressure) gas streams in a two-membrane permeator, namely, "perfect mixing," countercurent flow, and cocurrent flow. An analytical study of gas separation in such a permeator operating under "perfect mixing" conditions has been reported by Ohno et al. (1977). However, these investigators considered a permeator design yielding only two (permeated)

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product streams. The present study takes into account the possibility of extracting a third (unpermeated) product stream from the permeator.

Numerical solutions of the models developed here provide information on the extent of separation achievable in a two-membrane permeator and on the required membrane areas. Examples are presented for assumed selectivities (ideal separation factors) of the two membranes and for varying stage cuts. Many of the results of this study have been confirmed experimentally, as will be shown elsewhere. The usefulness of multi-membrane permeators is limited by the availability of membranes with sufficiently different gas selectivities. The membranes need not be prepared from solid polymers only, but can also be of the facilitated-transport type. The use of combinations of solid polymer and facilitated-transport membranes is also conceivable.

CONCLUSIONS AND SIGNIFICANCE

Mathematical models have been developed for the separation of binary gas mixtures by selective permeation through a permeator module housing two different types of membranes. The models are applicable to two-membrane permeators operating under "perfect mixing," countercurrent, and cocurrent flow conditions. The extent of gas separation and recovery of feed components in the two-membrane permeator, as well as the required membrane areas, depend on the following variables: the feed flow rate, the feed composition, the nature of the membranes, the temperature, the pressures of the permeated and unpermeated gas streams in the permeator, the "stage cuts," and the flow patterns of the permeated and unpermeated gas streams in the permeator ("perfect mixing," countercurrent, etc.).

The two-membrane permeator under consideration divides the feed into one unpermeated (high pressure) gas stream and two permeated (low pressure) gas streams, and therefore yields three product streams. The pressures of the three streams in the permeator can be varied independently of each other. Moreover, the permeator can operate at two independent stage cuts, one for each membrane (a "stage" cut is the fraction of the feed allowed to permeate through a membrane). The stage cuts can be varied by changing the membrane areas, at a fixed feed rate, or by changing the feed flow rate when the membrane areas are constant. In the latter case the stage cuts cannot be varied independently of each other.

The separation of a binary gas mixture by means of a two-membrane permeator, using two different types of membranes with hypothetical gas permeabilities, was studied as a function of the two stage cuts. The extent of separation, the component recovery, and the membrane area were determined from numerical solutions of the mathematical models for the three flow patterns mentioned above. It was found that a two-membrane permeator can yield a higher degree of separation and, in particular, a much higher degree of component recovery than a single-membrane permeator provided with one of the two membranes and operating under comparable conditions. Two-membrane permeators also have the advantage, as mentioned earlier, to separate multicomponent mixtures, if suitable membranes can be synthesized. For example, a ternary gas mixture can be separated in a two-membrane permeator into its three components, the component permeating the slowest through both membranes being concentrated in the unpermeated stream. The other two components are each concentrated in one of the permeated streams. This concept can be extended in principle to gas mixtures containing more than three components, but its application may be very limited because more than two membranes with different gas selectivities are then required.

This study also showed that, in general, countercurrent flow is the most efficient flow pattern, followed by cocurrent and "perfect mixing." In other words, countercurrent flow yields the highest degree of separation and requires the smallest membrane areas for a given feed rate. However, special conditions were found where the order of efficiency is reversed, "perfect mixing" being the most efficient flow pattern. In a single-membrane permeator, by contrast, countercurrent flow is always the most efficient flow pattern.

The above result suggests that, when constructing a two-membrane permeator module, it should not be taken for granted that countercurrent flow must always be used to achieve the highest separation. Rather, a combination of flow patterns may be best suited for this purpose. Although "perfect mixing" cannot be used in conjunction with any other flow pattern, it should be possible to devise a permeator embodying both cocurrent and countercurrent flow. For such a design, two-membrane permeator modules are most easily constructed when the membranes are available in the form of capillaries or hollow fibers.

GENERAL CONSIDERATIONS

The Single-Membrane Permeator

Gas mixtures are separated by selective permeation through polymer membranes in devices, or modules, usually called "permeators." A permeator is essentially a high pressure vessel containing the membrane in sheet form or, preferably, in the form of hollow fibers. The vessel is provided with the necessary valving and instrumentation for the measurement and control of operating variables, such as pressures and gas flow rates. Constructional details of permeators have been reported in the technical and patent literature (e.g., Stern, 1972; Hwang and Kammermeyer, 1975). From a chemical engineering viewpoint, permeators are elementary separation stages whose function is similar to that of, say, distillation trays; therefore, permeators are sometimes called "permeation stages." (A permeation stage can also consist of two or more permeators connected in parallel so as to receive the same feed and yield the same product compositions.)

A greatly simplified diagram of a permeator is shown in Figure 1. The permeator is represented in this figure as an enclosure that is separated into two compartments by a planar nonporous membrane. Consider the separation of a binary gas mixture of components A and B in this device. The mixture (the "feed") is introduced into one of the compartments of the permeator (lower compartment in Figure 1) at a desired molar flow rate $L_{i(R)}$ and at a con-

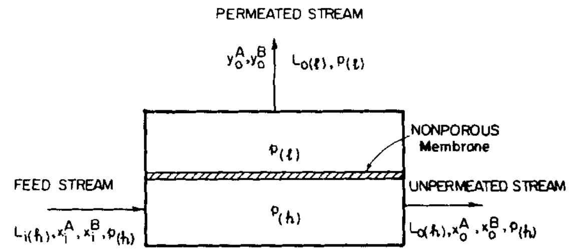

Figure 1. Single-membrane permeator.

stant total pressure $p_{(\hbar)}$. The mole fractions of components A and B in the feed are designated x_i^A and $x_i^B (= 1 - x_i^A)$, respectively. A fraction θ of the feed is allowed to permeate through the membrane into the second compartment (the upper compartment in Figure 1), which is maintained at a constant total pressure $p_{(\ell)}$ $(<p_{(\hbar)})$. The feed is thus partitioned into two product streams:

1) A permeated, low-pressure stream (the "permeate") enriched in the more rapidly permeating component of the feed, say component A.

2) An unpermeated, high-pressure product stream depleted in this component.

The molar flow rates of these product streams are designated hereafter $L_{o(\ell)}$ and $L_{o(\hbar)}$, respectively, and the corresponding mole fractions of component A in the two streams are designated y_o^A and x_o^A. Subscripts $\hbar$ and ℓ refer to the high- and low-pressure sides of the membrane, while subscripts i and o stand for stage inlet and outlet, respectively. The fraction θ of the feed that is allowed to permeate through the membrane is thus

$$\theta = L_{o(\ell)}/L_{i(\hbar)}; \tag{1}$$

θ is commonly called the "stage" cut.

The extent of separation achievable in a single-membrane permeator, or permeation stage, and the required membrane area (for a specified feed rate) depend on the following variables: the feed composition, the nature of the membrane, the temperature, the pressures $p_{(\hbar)}$ and $p_{(\ell)}$ on the membrane interfaces, the stage cut, and the flow patterns of the high and low pressure streams in the permeator (e.g., countercurrent, "perfect mixing," etc.). Methods of computing the compositions of the product streams and the membrane area have been discussed by Oishi et al. (1961), Stern and Walawender (1969), Walawender and Stern (1972), Hwang and Kammermeyer (1975), and Pan and Habgood (1974, 1978a,b).

The Two-Membrane Permeator

Ohno and coworkers (1976–78) have made the interesting suggestion that the separation of a gas mixture by selective permeation could be greatly enhanced by using more than one type of membrane, each type being preferentially permeable to a different component of the mixture. According to this concept, a binary mixture of components A and B is best separated in a permeator provided with two different types of membranes, which will be designated hereafter as membranes I and II; membrane I must be more permeable, for instance, to component A, while membrane II must be more permeable to component B. Hence, the two membranes must exhibit reversed selectivities toward the two components of the feed mixture. A diagram of a two-membrane permeator is shown in Figure 2.

As is evident from this figure, the high pressure feed is separated into three product streams:

1) A permeated stream of molar flow rate $L_{\mathrm{I}o(\ell)}$ and at pressure $p_{\mathrm{I}(\ell)}$ $(<p_{(\hbar)})$, produced by membrane I and enriched in component A.

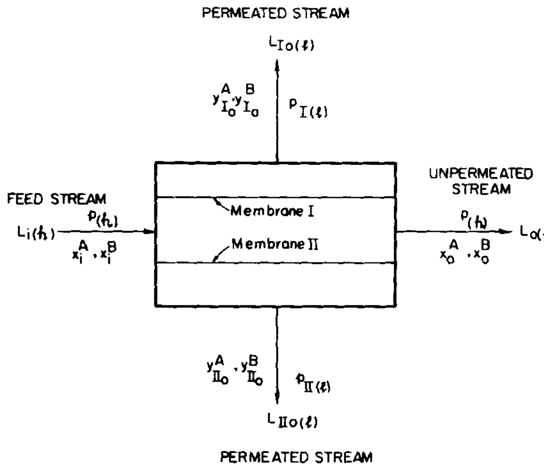

Figure 2. Two-membrane permeator.

2) A permeated stream of molar flow rate $L_{\mathrm{II}o(\ell)}$ and pressure $p_{\mathrm{II}(\ell)}$ $(<p_{(\hbar)})$, produced by membrane II and depleted in component A, i.e., enriched in component B.

3) An unpermeated stream of molar flow rate $L_o(\hbar)$ and at pressure $p_{(\hbar)}$, which can be either enriched or depleted in component A.

The mole fractions of component A in these product streams will be designated $y_{\mathrm{I}o}^A$, $y_{\mathrm{II}o}^A$, and x_o^A, respectively.

The extent of separation achievable in a two-membrane permeator and the required membrane areas depend on the same operating variables as in a single-membrane permeator, except that one has to consider two independent stage cuts and (if necessary) two different $p_{(\ell)}$ values, one for each membrane. The stage cuts are defined by the relations

$$\theta_{\mathrm{I}} = L_{\mathrm{I}o(\ell)}/L_{i(\hbar)}, \quad \text{for membrane I} \tag{2}$$

$$\theta_{\mathrm{II}} = L_{\mathrm{II}o(\ell)}/L_i(\hbar), \quad \text{for membrane II} \tag{3}$$

Flow Patterns

The following flow patterns in single-membrane permeators have been studied extensively by a number of investigators. These flow patterns are also of interest for gas separation in two-membrane permeators.

"Perfect-Mixing" Conditions. "Perfect mixing" in a permeator is defined as the limiting condition when the compositions of the gas streams on the high- or low-pressure sides of the membrane are uniform and the same as those of the corresponding product streams leaving the permeator. The separation of binary gas mixtures in a single-membrane permeator under such conditions was first studied by Weller and Steiner (1950a, b). This study was extended to the separation of multicomponent mixtures by Stern et al. (1965).

The first analytical study of gas separation in a perfectly-mixed two-membrane permeator was reported by Ohno et al. (1977). However, these investigators considered only the case when $L_{o(\hbar)} = 0$; the composition of the unpermeated gas mixture on the high-pressure side of the membranes is then the same as the feed composition. The calculation of the product compositions in this case is relatively simple. Sirkar (1980) reexamined Ohno's method for $L_{o(\hbar)} \neq 0$, but with the simplifying assumption that the pressures $p_{\mathrm{I}(\ell)}$ and $p_{\mathrm{II}(\ell)}$ are much lower than $p_{(\hbar)}$. These studies of Ohno et al. and Sirkar were made with reference to binary mixtures. More recently, Sengupta and Sirkar (1983) studied the separation of multicomponent gas mixtures in a two-membrane permeator.

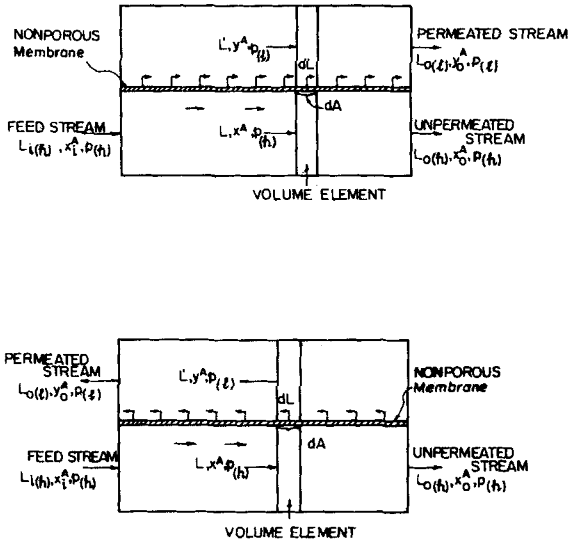

Figure 3. Single-membrane permeator with (a) cocurrent and (b) countercurrent flow.

Cocurrent and Countercurrent Flow. For these flow patterns, which are illustrated in Figure 3, the high- and low-pressure streams in the permeator flow along the membrane either cocurrently or countercurrently to one another. It is assumed that no mixing takes place in either stream. Oishi et al. (1961) studied the separation of binary gas mixtures by gaseous diffusion across single porous barriers under both cocurrent and countercurrent conditions. This analysis was later extended by other investigators to gas permeation through nonporous polymer membranes in single-membrane permeators (Walawender and Stern, 1972; Blaisdell and Kammermeyer, 1973; Stern and Wang, 1978). No analyses of gas separation in cocurrent or countercurrent two-membrane permeators appear to have been reported in the literature. Therefore, the present study was devoted to such analyses. Only the separation of binary gas mixtures has been considered up to now, but the methods used can be extended to multicomponent mixtures.

THEORETICAL CONSIDERATIONS

The extent of separation and membrane area requirements in a two-membrane permeator can be calculated for "perfect mixing," cocurrent, and countercurrent flow conditions as follows.

"Perfect-Mixing" Conditions

The analysis of gas separation in a two-membrane permeator under "perfect-mixing" conditions closely follows that presented by Stern and Walawender (1969) for a single-membrane permeator. The permeation, or transport, of gases through the types of membranes of interest in this study is controlled by Fickian diffusion of the penetrant gases in the polymer matrix (Stern and Frisch, 1981).

Consider the isothermal, steady-state permeation of a binary gas mixture of components A and B through two homogeneous, isotropic, and planar membranes. The two membranes, designated I and II, are housed in the same permeator, as shown in Figure 2. In order to determine the extent of separation of the mixture achievable in the two-membrane permeator, Fick's first law is written for each component of the mixture and for each membrane. For the stated conditions, Fick's law becomes:

For membrane I:

$$y_{Io}^{A} L_{Io(\ell)} = (\bar{P}_{I}^{A} A_{I}/\delta_{I})[p_{(h)} x_{o}^{A} - p_{I(\ell)} y_{Io}^{A}] \tag{4a}$$

$$y_{Io}^{B} L_{Io(\ell)} = (1 - y_{Io}^{A}) L_{Io(\ell)} = (\bar{P}_{I}^{B} A_{I}/\delta_{I})[p_{(h)}(1 - x_{o}^{A}) - p_{I(\ell)}(1 - y_{Io}^{A})] \tag{4b}$$

For membrane II:

$$y_{IIo}^{A} L_{IIo(\ell)} = (\bar{P}_{II}^{A} A_{II}/\delta_{II})[p_{(h)} x_{o}^{A} - p_{II(\ell)} y_{IIo}^{A}] \tag{5a}$$

$$(1 - y_{IIo}^{A}) L_{IIo(\ell)} = (\bar{P}_{II}^{B} A_{II}/\delta_{II})[p_{(h)}(1 - x_{o}^{A}) - p_{II(\ell)}(1 - y_{IIo}^{A})] \tag{5b}$$

where y_{o}^{A} and y_{o}^{B} are the mole fractions of components A and B in the permeate streams; x_{o}^{A} is the mole fraction of component A in the unpermeated stream; $L_{o(\ell)}$ is the flow rate of the permeated streams; $p_{(\ell)}$ is the total pressure on the low-pressure side of the membranes; $p_{(h)}$ is the total pressure on the high-pressure side of the membranes; A and δ are the area and thickness of the membranes; $\bar{P}^{A}$ and $\bar{P}^{B}$ are the mean permeability coefficients of components A and B; and the subscripts I and II refer to membranes I and II. The symbols in the above equations are also indicated in Figure 2.

A material balance around the entire permeator can be written as

$$L_{i(h)} x_{i}^{A} = L_{Io(\ell)} y_{Io}^{A} + L_{IIo(\ell)} y_{IIo}^{A} + L_{o(h)} x_{o}^{A} \tag{6}$$

or

$$x_{i}^{A} = \theta_{I} y_{Io}^{A} + \theta_{II} y_{IIo}^{A} + \theta_{o} x_{o}^{A} \tag{7}$$

where θ_{I} and θ_{II} are the stage cuts defined by Eqs. 2 and 3, and where $\theta_{o} = 1 - \theta_{I} - \theta_{II} = L_{o(h)}/L_{i(h)}$.

Expressions relating y_{Io}^{A} and y_{IIo}^{A} to x_{o}^{A} can be obtained by first dividing Eqs. 4a and 5a by Eqs. 4b and 5b, respectively. Thus

$$y_{Io}^{A}/(1 - y_{Io}^{A}) = \alpha_{I}^{*} \frac{r_{I} x_{o}^{A} - y_{Io}^{A}}{r_{I}(1 - x_{o}^{A}) - (1 - y_{Io}^{A})} \tag{8a}$$

$$y_{IIo}^{A}/(1 - y_{IIo}^{A}) = \alpha_{II}^{*} \frac{r_{II} x_{o}^{A} - y_{IIo}^{A}}{r_{II}(1 - x_{o}^{A}) - (1 - y_{IIo}^{A})} \tag{8b}$$

where

$$\alpha_{I}^{*} = \bar{P}_{I}^{A}/\bar{P}_{I}^{B}$$
$$\alpha_{II}^{*} = \bar{P}_{II}^{A}/\bar{P}_{II}^{B}$$
$$r_{I} = p(h)/p_{I}(\ell)$$
$$r_{II} = p_{(h)}/p_{II(\ell)}$$

where r is the ratio of pressures on the two sides of the membrane, and α^{*} is the ideal separation factor (Stern and Walawender, 1969). Equations 8a and 8b can be rearranged to yield quadratic equations for y_{Io}^{A} and y_{IIo}^{A} as a function of x_{o}^{A}; the solutions of the latter are

$$y_{Io}^{A} = (-b_{I} \pm [b_{I}^{2} - 4a_{I}c_{I}]^{1/2})/2a_{I} \tag{9a}$$

$$y_{IIo}^{A} = (-b_{II} \pm [b_{II}^{2} - 4a_{II}c_{II}]^{1/2})/2a_{II} \tag{9b}$$

where

$$a_{I} = (\alpha_{I}^{*} - 1)$$
$$b_{I} = -\{r_{I} + (\alpha_{I}^{*} - 1)(r_{I} x_{o}^{A} + 1)\}$$
$$c_{I} = \alpha_{I}^{*} r_{I} x_{o}^{A}$$

and

$$a_{II} = (\alpha_{II}^{*} - 1)$$
$$b_{II} = -\{r_{II} + (\alpha_{II}^{*} - 1)(r_{II} x_{o}^{A} + 1)\}$$
$$c_{II} = \alpha_{II}^{*} r_{II} x_{o}^{A}$$

Only the negative root in Eqs. 9a and 9b is physically meaningful (Walawender and Stern, 1972).

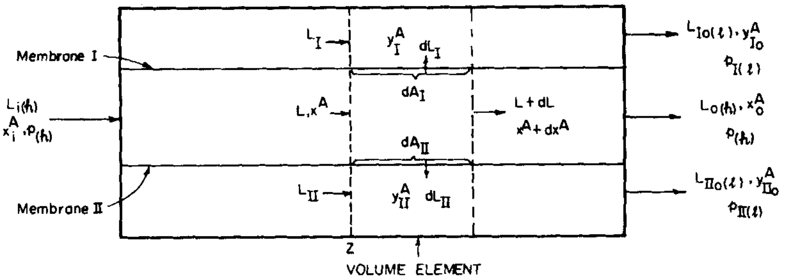

Figure 4. Two-membrane permeator with cocurrent flow pattern.

In order to determine the compositions of the permeated streams and the membrane areas, the following computational procedure may be employed:

1. Specify the values of x_i^A, $p_{(h)}$, $L_{i(h)}$, $p_{I(\ell)}$, $p_{II(\ell)}$, $\bar{P}_I^A$, $\bar{P}_I^B$, $\bar{P}_{II}^A$, $\bar{P}_{II}^B$, δ_I, δ_{II}, θ_I, and θ_{II}.
2. Calculate α_I^* $(=\bar{P}_I^A/\bar{P}_I^B)$, α_{II}^* $(=\bar{P}_{II}^A/\bar{P}_{II}^B)$, r_I $(=p_{(h)}/p_{I(\ell)})$, and r_{II} $(=p_{(h)}/p_{II(\ell)})$.
3. Assume a value of x_o^A and calculate y_{Io}^A and y_{IIo}^A from Eqs. 9a and 9b.
4. Recalculate x_o^A from the material balance, Eq. 7.

If the calculated value of x_o^A is different from its assumed value, recompute the permeate concentrations assuming a new value of x_o^A. Continue the iteration until the calculated and assumed values of x_o^A converge.

The areas of membranes I and II are determined from Eqs. 4a and 5a or from Eqs. 4b and 5b, respectively.

Cocurrent Flow

The separation of a gas mixture in a two-membrane permeator under cocurrent conditions is illustrated in Figure 4. It is seen that both permeated (low-pressure) streams flow in the same direction as the unpermeated (high-pressure) stream. The total and component material balances around the permeator from the feed inlet to some position z are represented by the following equations:

$$L_{i(h)} = L_I + L_{II} + L \tag{10a}$$

$$L_{i(h)}x_i^A = L_I y_I^A + L_{II} y_{II}^A + Lx^A \tag{10b}$$

$$L_{i(h)}(1 - x_i^A) = L_I(1 - y_I^A) + L_{II}(1 - y_{II}^A) + L(1 - x^A) \tag{10c}$$

A component material balance around a differential volume element of the permeator also yields

$$0 = d[L_I y_I^A] + d[L_{II} y_{II}^A] + d[Lx^A] \tag{10d}$$

$$0 = d[L_I(1 - y_I^A)] + d[L_{II}(1 - y_{II}^A)] + d[L(1 - x^A)] \tag{10e}$$

In the above equations, L_I and L_{II} are the local molar flow rates of the permeated streams from membranes I and II, y_I^A and y_{II}^A are the corresponding local concentrations of component A in these streams, and L and x^A are the local molar flow rate of the unpermeated stream and the concentration of component A in that stream, respectively. The other symbols are as used before (cf. Figure 4).

In addition, the local molar fluxes of components A and B through a differential membrane area dA_I are given by the relations

$$d[L_I y_I^A] = (\bar{P}_I^A/\delta_I)[p_{(h)}x^A - p_{I(\ell)}y_I^A]dA_I = C_I^A dA_I \tag{11}$$

$$d[L_I(1 - y_I^A)] = (\bar{P}_I^B/\delta_I)[p_{(h)}(1 - x^A) - p_{I(\ell)}(1 - y_I^A)]dA_I = C_I^B dA_I \tag{12}$$

Similarly, the molar fluxes of components A and B through a differential membrane area dA_{II} are

$$d[L_{II} y_{II}^A] = (\bar{P}_{II}^A/\delta_{II})[p_{(h)}x^A - p_{II(\ell)}y_{II}^A]dA_{II} = C_{II}^A dA_{II} \tag{13}$$

$$d[L_{II}(1 - y_{II}^A)] = (\bar{P}_{II}^B/\delta_{II})[p_{(h)}(1 - x^A) - p_{II(\ell)}(1 - y_{II}^A)]dA_{II} = C_{II}^B dA_{II} \tag{14}$$

(C represents a function of the mole fraction concentrations x and y.)

Without loss of generality, it can be assumed that the differential areas are related by a constant, i.e., $dA_{II} = RdA_I$. More specifically, if the two membranes are in the form of hollow fibers of equal length, this constant is the ratio of the number of fibers N of each kind and of their respective diameters D:

$$R = (N_{II} \cdot D_{II})/(N_I \cdot D_I) \tag{15}$$

Inserting the expression for $d[L_I y_I^A]$ and $d[L_{II} y_{II}^A]$ into Eq. 10d yields for component A

$$\begin{aligned} -d[Lx^A] &= C_I^A dA_I + C_{II}^A dA_{II} \\ &= (C_I^A + RC_{II}^A)dA_I \\ &= C^A dA_I \end{aligned} \tag{16}$$

Similarly, for component B

$$\begin{aligned} -d[L(1 - x^A)] &= (C_I^B + RC_{II}^B)dA_I \\ &= C^B dA_I \end{aligned} \tag{17}$$

The following identities are introduced:

$$Ldx^A = (1 - x^A)d[Lx^A] - x^A d[L(1 - x^A)] \tag{18a}$$

$$L_I dy_I^A = (1 - y_I^A)d[L_I y_I^A] - y_I^A d[L_I(1 - y_I^A)] \tag{18b}$$

$$L_{II} dy_{II}^A = (1 - y_{II}^A)d[L_{II} y_{II}^A] - y_{II}^A d[L_{II}(1 - y_{II}^A)] \tag{18c}$$

The quantities on the righthand side of each identify are given by Eqs. 11 to 14, 16, and 17. Accordingly

$$-Ldx^A = (1 - x^A)C^A\, dA_I - x^A C^B\, dA_I \tag{19a}$$

$$L_I dy_I^A = (1 - y_I^A)C_I^A dA_I - y_I^A C_I^A\, dA_I \tag{19b}$$

$$L_{II} dy_{II}^A = (1 - y_{II}^A)RC_{II}^A dA_I - y_{II}^A RC_{II}^B\, dA_I \tag{19c}$$

The above three equations may be rearranged to yield

$$dx^A/dA_I = -[(1 - x^A)C^A - x^A C^B]/L \tag{20a}$$

$$dy_I^A/dA_I = [(1 - y_I^A)C_I^A - y_I^A C_I^B]/L_I \tag{20b}$$

$$dy_{II}^A/dA_I = R[(1 - y_{II}^A)C_{II}^A - y_{II}^A C_{II}^B]/L_{II} \tag{20c}$$

If Eq. 16 is added to Eq. 17, the following expression is obtained:

$$dL/dA_I = -(C^A + C^B) \tag{21}$$

Similar expressions for L_I and L_{II} can be derived:

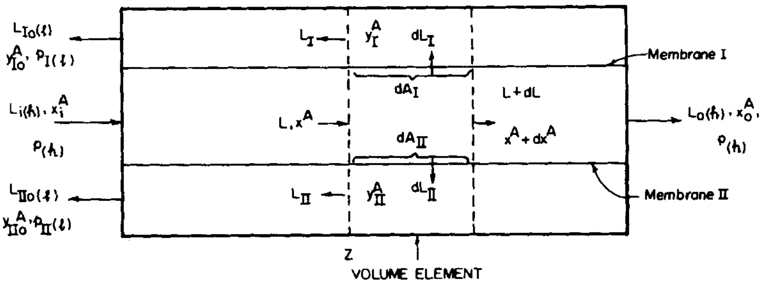

Figure 5. Two-membrane permeator with countercurrent flow pattern.

$$dL_{\mathrm{I}}/dA_{\mathrm{I}} = C_{\mathrm{I}}^A + C_{\mathrm{I}}^B \tag{22a}$$

$$dL_{\mathrm{II}}/dA_{\mathrm{I}} = R(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B) \tag{22b}$$

With L_{II} as the independent variable, the rearrangement of Eqs. 19–22 yields differential equations for A_{I}, y_{I}^A, y_{II}^A, L, L_{I}, and x^A as

$$dA_{\mathrm{I}}/dL_{\mathrm{II}} = 1/[R(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)] \tag{23a}$$

$$dy_{\mathrm{I}}^A dL_{\mathrm{II}} = [(1 - y_{\mathrm{I}}^A)C_{\mathrm{I}}^A - y_{\mathrm{I}}^A C_{\mathrm{I}}^B]/RL_{\mathrm{I}}(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B) \tag{23b}$$

$$dy_{\mathrm{II}}^A/dL_{\mathrm{II}} = [(1 - y_{\mathrm{II}}^A)C_{\mathrm{II}}^A - y_{\mathrm{II}}^A C_{\mathrm{II}}^B]/L_{\mathrm{II}}(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)] \tag{23c}$$

$$dx^A/dL_{\mathrm{II}} = -[(1 - x^A)C^A - x^A C^B]/[RL(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)] \tag{23d}$$

$$dL/dL_{\mathrm{II}} = -[C^A + C^B]/[R(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)] \tag{23e}$$

$$dL_{\mathrm{I}}/dL_{\mathrm{II}} = [C_{\mathrm{I}}^A + C_{\mathrm{I}}^B]/[R(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)] \tag{23f}$$

These equations can be simultaneously integrated from $L_{\mathrm{II}} = 0$ (inlet) to $L_{\mathrm{II}} = L_{\mathrm{II}o(\ell)}$ (outlet) using an appropriate numerical technique. In previous studies of single-membrane permeators, x^A has generally been used as the variable of integration. However, it is conceivable that under certain operating conditions the unpermeated product concentration x_o^A can be equal to x_i^A for a two-membrane permeator. To overcome the problem of integration that arises (i.e., $dx^A = 0$ along the length of the permeator), L_{II} is used as the variable of integration, since it must increase from zero to some finite value.

The boundary conditions at the permeator inlet are

$$x^A = x_i^A \qquad L = L_{i(h)}$$
$$y_{\mathrm{I}}^A = y_{\mathrm{I}i}^A \qquad L_{\mathrm{I}} = 0$$
$$y_{\mathrm{II}}^A = y_{\mathrm{II}i}^A \qquad L_{\mathrm{II}} = 0$$
$$A_{\mathrm{I}} = A_{\mathrm{II}} = 0$$

The boundary conditions at the permeator outlet are

$$x^A = x_o^A \qquad L = L_{o(h)} = \theta_o L_{i(h)}$$
$$y_{\mathrm{I}}^A = y_{\mathrm{I}o}^A \qquad L_I = L_{\mathrm{I}o(\ell)} = \theta_{\mathrm{I}} L_{i(h)}$$
$$y_{\mathrm{II}}^A = y_{\mathrm{II}o}^A \qquad L_{\mathrm{II}} = L_{\mathrm{II}o(\ell)} = \theta_{\mathrm{II}} L_{i(h)}$$

The initial permeate concentrations $y_{\mathrm{I}i}^A$ and $y_{\mathrm{II}i}^A$ are determined from the ratios of Eqs. 11 to 13 and 12 to 14, respectively, which are evaluated at the inlet:

$$y_{\mathrm{I}i}^A = (b_{\mathrm{I}} - [b_{\mathrm{I}}^2 - 4a_{\mathrm{I}}c_{\mathrm{I}}]^{1/2})/2a_{\mathrm{I}} \tag{24a}$$

$$y_{\mathrm{II}i}^A = (b_{\mathrm{II}} - [b_{\mathrm{II}}^2 - 4a_{\mathrm{II}}c_{\mathrm{II}}]^{1/2})/2a_{\mathrm{II}} \tag{24b}$$

where

$$a_{\mathrm{I}} = (\alpha_{I}^* - 1)$$
$$b_{\mathrm{I}} = r_{\mathrm{I}} + (\alpha_{\mathrm{I}}^* - 1)(r_{\mathrm{I}} x_i^A + 1)$$
$$c_{\mathrm{I}} = \alpha_{\mathrm{I}}^* r_{\mathrm{I}} x_i^A$$

and

$$a_{\mathrm{II}} = (\alpha_{\mathrm{II}}^* - 1)$$
$$b_{\mathrm{II}} = r_{\mathrm{II}} + (\alpha_{\mathrm{II}}^* - 1)(r_{\mathrm{II}} x_i^A + 1)$$
$$c_{\mathrm{II}} = \alpha_{\mathrm{II}}^* r_{\mathrm{II}} x_i^A$$

Both $dy_{\mathrm{I}}^A/dL_{\mathrm{II}}$ and $dy_{\mathrm{II}}^A/dL_{\mathrm{II}}$ are indeterminate at the inlet; therefore, L'Hospital's rule is applied to yield

$$\frac{dy_{\mathrm{I}}^A}{dL_{\mathrm{II}}} = \left.\frac{dy_{\mathrm{I}}^A}{dx^A}\right|_i \cdot \left.\frac{dx^A}{dL_{\mathrm{II}}}\right|_i = \left.\frac{(\overline{P}_{\mathrm{I}}^A/\delta_{\mathrm{I}})[1 - y_{\mathrm{I}}^A + y_{\mathrm{I}}^A(\overline{P}_{\mathrm{I}}^B/\overline{P}_{\mathrm{I}}^A)]p_{(h)}}{2(C_{\mathrm{I}}^A + C_{\mathrm{I}}^B) + (\overline{P}_{\mathrm{I}}^A/\delta_{\mathrm{I}})[1 - y_{\mathrm{I}}^A + y_{\mathrm{I}}^A(\overline{P}_{\mathrm{I}}^B/\overline{P}_{\mathrm{I}}^A)p_{\mathrm{I}(\ell)}}\right| \cdot \left.\frac{dx^A}{dL_{\mathrm{II}}}\right|_i \tag{25}$$

and

$$\frac{dy_{\mathrm{II}}^A}{dL_{\mathrm{II}}} = \left.\frac{dy_{\mathrm{II}}^A}{dx^A}\right|_o \left.\frac{dx^A}{dL_{\mathrm{II}}}\right|_i = \left.\frac{(\overline{P}_{\mathrm{II}}^A/\delta_{\mathrm{II}})[1 - y_{\mathrm{II}}^A + y_{\mathrm{II}}^A(\overline{P}_{\mathrm{II}}^B/\overline{P}_{\mathrm{II}}^A)]p_{(h)}}{2(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B) + (\overline{P}_{\mathrm{II}}^A/\delta_{\mathrm{II}})[1 - y_{\mathrm{II}}^A + y_{\mathrm{II}}^A + y_{\mathrm{II}}^A(\overline{P}_{\mathrm{II}}^B/\overline{P}_{\mathrm{II}}^A)]p_{\mathrm{II}(\ell)}}\right|_i \cdot \left.\frac{dx^A}{dL_{\mathrm{II}}}\right|_i \tag{26}$$

Countercurrent Flow

Countercurrent flow in a two-membrane permeator is illustrated in Figure 5. The mass balance around the permeator from its outlet to a position z yields

$$L = L_{\mathrm{I}} + L_{\mathrm{II}} + L_{o(h)} \tag{27a}$$

$$Lx^A = L_{\mathrm{I}}y_{\mathrm{I}}^A + L_{\mathrm{II}}y_{\mathrm{II}}^A + L_{o(h)}x_o^A \tag{27b}$$

$$L(1 - x^A) = L_{\mathrm{I}}(1 - y_{\mathrm{I}}^A) + L_{\mathrm{II}}(1 - y_{\mathrm{II}}^A) + L_{o(h)}(1 - x_o^A) \tag{27c}$$

$$d[Lx^A] = d[L_{\mathrm{I}}y_{\mathrm{I}}^A] + d[L_{\mathrm{II}}y_{\mathrm{I}}^A] \tag{27d}$$

$$d[L(1 - x^A)] = d[L_{\mathrm{I}}(1 - y_{\mathrm{I}}^A)] + d[L_{\mathrm{II}}(1 - y_{\mathrm{II}}^A)] \tag{27e}$$

In addition, the equations for the molar fluxes of components A and B, using the quantities defined above, are

$$-d[L_{\mathrm{I}}y_{\mathrm{I}}^A] = C_{\mathrm{I}}^A dA_{\mathrm{I}} \tag{28a}$$

$$-d[L_{\mathrm{II}}y_{\mathrm{II}}^A] = R\, C_{\mathrm{II}}^A\, dA_{\mathrm{I}} \tag{28b}$$

$$-d[L_{\mathrm{I}}(1 - y_{\mathrm{I}}^A)] = C_{\mathrm{I}}^B\, dA_{\mathrm{I}} \tag{28c}$$

$$-d[L_{\mathrm{II}}(1 - y_{\mathrm{II}}^A)] = R\, C_{\mathrm{II}}^B\, dA_{\mathrm{I}} \tag{28d}$$

Thus

$$d[Lx^A] = -C^A\, dA_{\mathrm{I}} \tag{29a}$$

$$d[L(1 - x^A)] = -C^B\, dA_{\mathrm{I}} \tag{29b}$$

The general differential equations that govern countercurrent flow are derived in exactly the same manner as cocurrent flow. Hence, using L as the independent variable rather than L_{II}, the differential equations expressing the change in y_{I}^A, y_{II}^A, x^A, A_{I}, L_I, and L_{II} with varying L are

$$dA_{\mathrm{I}}/dL = -1/(C^A + C^B) \tag{30a}$$

$$dy_{\mathrm{I}}^A/dL = [(1 - y_{\mathrm{I}}^A)C_{\mathrm{I}}^A - y_{\mathrm{I}}^A C_{\mathrm{I}}^B]/[L_{\mathrm{I}}(C^A + C^B)] \tag{30b}$$

$$dy_{\mathrm{II}}^A/dL = R[(1 - y_{\mathrm{II}}^A)C_{\mathrm{II}}^A - y_{\mathrm{II}}^A C_{\mathrm{II}}^B]/[L_{\mathrm{II}}(C^A + C^B)] \tag{30c}$$

$$dx^A/dL = [(1 - x^A)C_{\mathrm{I}}^A + x^A C_{\mathrm{I}}^B]/L(C^A + C^B)] \tag{30d}$$

$$dL_{\mathrm{I}}/dL = (C_{\mathrm{I}}^A + C_{\mathrm{I}}^B)/(C^A + C^B) \tag{30e}$$

$$dL_{\mathrm{II}}/dL = R(C_{\mathrm{II}}^A + C_{\mathrm{II}}^B)/(C^A + C^B) \tag{30f}$$

The boundary conditions at the permeator outlet are

$x^A = x_o^A$	$A_{\mathrm{I}} = A_{\mathrm{II}} = 0$
$y_{\mathrm{I}}^A = y_{\mathrm{I}i}^A$	$y_{\mathrm{II}}^A = y_{\mathrm{II}i}^A$
$L_{\mathrm{I}} = L_{\mathrm{II}} = 0$	$L = L_{o(h)}$

Further, the boundary conditions at the permeator inlet are

$x^A = x_i^A$	$L = L_{i(h)}$
$y_{\mathrm{I}}^A = y_{\mathrm{I}o}^A$	$L_{\mathrm{I}} = L_{\mathrm{I}o(\ell)}$
$y_{\mathrm{II}}^A = y_{\mathrm{II}o}^A$	$L_{\mathrm{II}} = L_{\mathrm{II}o(\ell)}$

dy_{I}^A/dL and dy_{II}^A/dL, which are indeterminate at the outlet, are obtained by multiplying Eqs. 25 and 26 by dL_{II}/dL.

To begin the integration from the permeator outlet, $L_{o(h)}$ and x_o^A must first be specified. If the parameter R is assigned a certain value, then only one stage cut, either θ_{I} or θ_{II}, can be fixed so that the system is not overspecified. In this study the solution of the differential equations involves the following trial-and-error procedure for determining the two variables x_o^A and θ_{I}:

1. A value is assumed for x_o^A, the mole fraction of component A in the unpermeated (high-pressure) stream at the permeator outlet.
2. With the stage cut θ_{II} specified, θ_{I} is arbitrarily chosen (such that $\theta_{\mathrm{I}} + \theta_{\mathrm{II}} < 1$). $L_{o(h)}$ is determined from the mass balance around the permeator.
3. The integration of Eqs. 30a–f is carried out from $L = L_{o(h)}$ to $L_{i(h)}$. If θ_{I} and x_o^A are chosen correctly, then the correct values of x^A, L_I, and L_{II} will be obtained, i.e., x_o^A, $L_{\mathrm{I}o(\ell)}$, and $L_{\mathrm{II}o(\ell)}$.
4. If these conditions are not satisfied, a new set of values are selected for x_o^A and $L_{o(h)}$, using a gradient method for multivariable search (Beveridge and Schechter, 1975) until the following objective functions are satisfied:

$$\left|\frac{x_{i\,\mathrm{specified}}^A - x_{i\,\mathrm{calc}}^A}{x_{i\,\mathrm{specified}}^A}\right|,\ \left|\frac{L_{\mathrm{I}o(\ell)\,\mathrm{specified}} - L_{\mathrm{I}o(\ell)\,\mathrm{calc}}}{L_{\mathrm{I}o(\ell)\,\mathrm{specified}}}\right| \leqslant 10^{-5}$$

The integration of Eqs. 23a–f and 30a–f was carried out in this work by the use of GEARB, an integration package developed by Hindmarsh (1975).

RESULTS OF COMPUTATIONS

Test of Programs

Three computer programs were developed, based on the above mathematical models, for calculating the separation of a binary gas mixture in a two-membrane permeator for "perfect mixing," cocurrent, and countercurrent flow patterns. The programs were tested for reliability by calculating the extent of separation of a binary gas mixture under conditions where the two-membrane permeator behaves like a single-membrane permeator and by comparing the results of the calculations with those reported in the literature for the latter device. The two-membrane permeator behaves like a single-membrane permeator when:

(1) Membranes I and II in the two-membrane permeator exhibit the same permeation behavior toward the two components of a gas mixture; i.e., membrane I and II are identical.

(2) One of the membranes is impermeable to all components of the gas mixture or, which is equivalent, the stage cut for that membrane is zero.

The above conditions yield the same results insofar as the extent of separation is concerned, but the membrane area for condition 1 is twice as large as that for condition 2.

Stern and Walawender (1969, 1972) have reported the results of a parametric study on the separation of air in a single-membrane

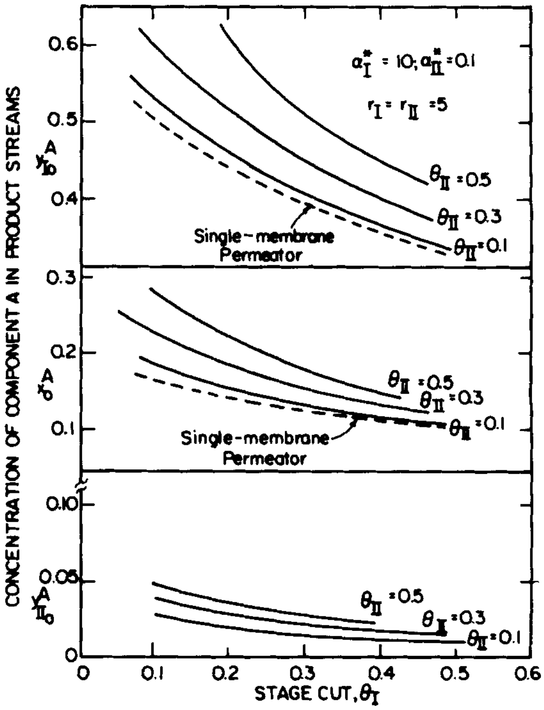

Figure 6. Separation of a binary gas mixture in a two-membrane permeator. Concentration of component A in product streams as a function of stage cuts θ_{I} and θ_{II} ("perfect-mixing" conditions).

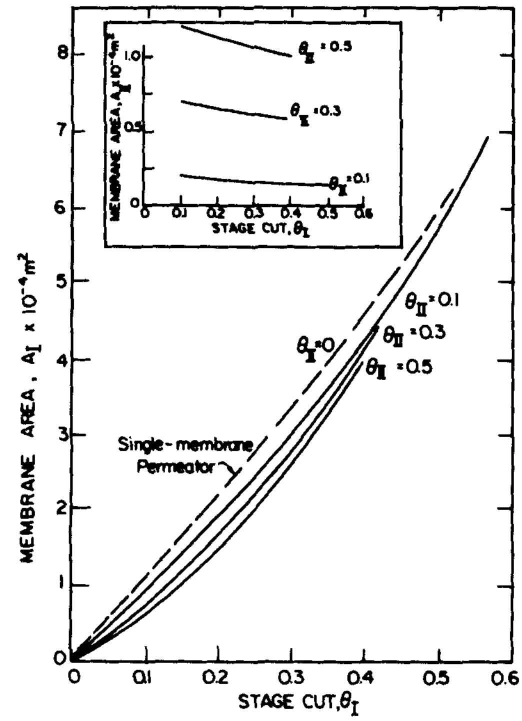

Figure 7. Separation of a binary gas mixture in a two-membrane permeator. Membrane area requirements as a function of stage cuts θ_I and θ_{II} ("perfect-mixing" conditions).

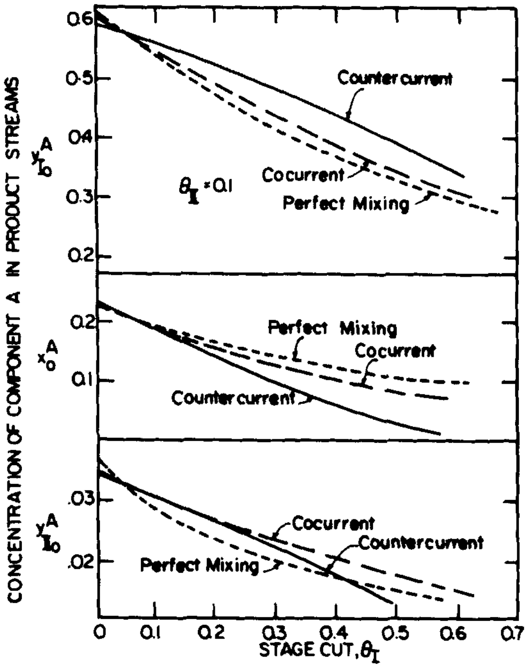

Figure 9. Separation of a binary gas mixture in a two-membrane permeator Concentration of component A in product streams as a function of stage cut θ_I and flow pattern. $\theta_{II} = 0.1$.

permeator for "perfect mixing," cocurrent, and countercurrent flow. These investigators assumed air to be a binary mixture of 20.9% O_2 and 79.1% N_2 and employed the following parameters in their calculations:

$$\bar{P}^{O_2} = 5.35 \times 10^{-15} \text{ [kg·m/(s·m}^2\text{·Pa)]}$$

(Permeability coefficients are customarily reported in the literature in units of cm³(STP)·cm/(s·cm²·cm Hg); these units are multiplied by 3.3464 × 10^{-9} M, where M is the molecular weight of the penetrant gas, to obtain SI units; thus

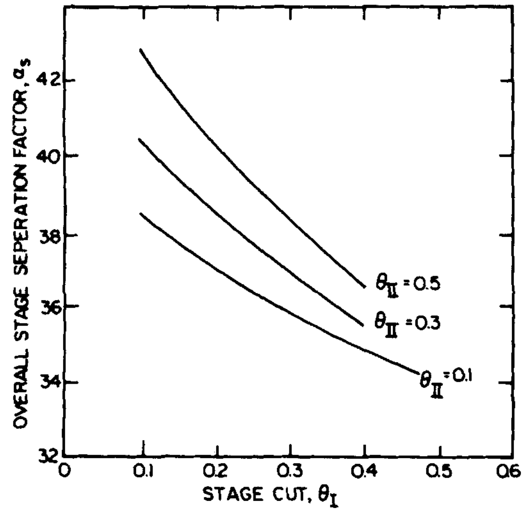

Figure 8. Separation of a binary gas mixture in a two-membrane permeator. Stage separation factor as a function of stage cuts θ_I and θ_{II} ("perfect-mixing" conditions).

$\bar{P}^{O_2} = 5 \times 10^{-8}$ [cm³(STP)·cm/(s·cm²·cm Hg)])

$\bar{P}^{N_2} = 2.34, 0.937$, and 0.468×10^{-15} [kg·m/(s·m²·Pa)]
(2.5, 1.0,. and 0.5 × 10^{-8} [cm³(STP)·cm/(s·cm²·cm Hg)])

$\alpha^*(\equiv \bar{P}^A/\bar{P}^B) = 2, 5$, and 10

$L_{t(h)} = 1$ m³(STP)/s (~1 ton air/d)

$p_{(h)} = 1 \times 10^5$ N/m² (76 cm Hg)

$r(\equiv p_{(h)}/p_{(\ell)}) = 5$ and 10

$\delta = 25.4$ μm (1 mil)

In order to test the reliability of the computer programs for the two-membrane permeator, it was assumed that membranes I and II are identical and that $\bar{P}^{O_2}$ and $\bar{P}^{N_2}$ for these membranes have the hypothetical values listed above. In a second test, the values of $\bar{P}^{O_2}$ and $\bar{P}^{N_2}$ listed above were used for membrane I, whereas membrane II was taken to be essentially impermeable to oxygen and nitrogen. The impermeability of membrane II to these gases was simulated by assuming values of $\bar{P}^{O_2}$ and $\bar{P}^{N_2}$ that were 10 orders of magnitude lower than those for membrane I. As mentioned earlier, a two-membrane permeator would behave under the conditions of the two tests like a single-membrane permeator. Other parameters, e.g., flow rate, necessary for the tests were also taken to be the same as those listed above. The separation of air was then determined with the three computer programs for the stated ideal separation factors and pressure ratios, and for a wide range of stage cuts. The compositions of the product streams were found to agree with the results reported by Walawender and Stern to within three decimal places, and the corresponding membrane areas were in agreement to within 2%.

Two-Membrane Permeators

1. *Perfect-Mixing" Conditions.* It was mentioned previously that the extent of separation of a gas mixture in a two-membrane

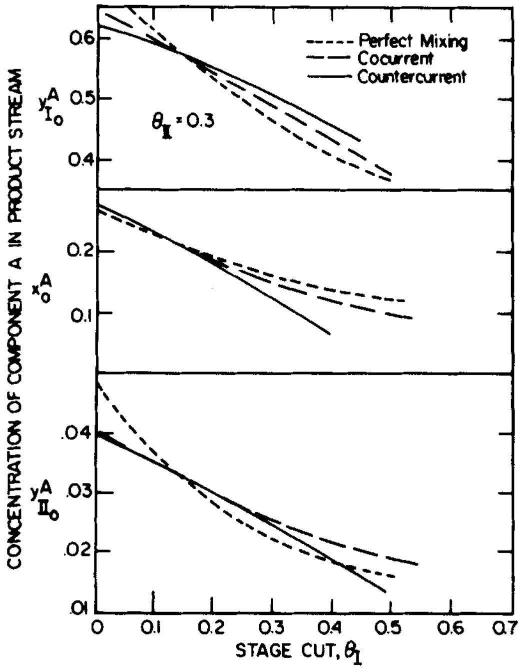

Figure 10. Separation of a binary gas mixture in a two-membrane permeator. Concentration of component A in product streams as a function of stage cut θ_I and flow pattern. θ_{II} = 0.3.

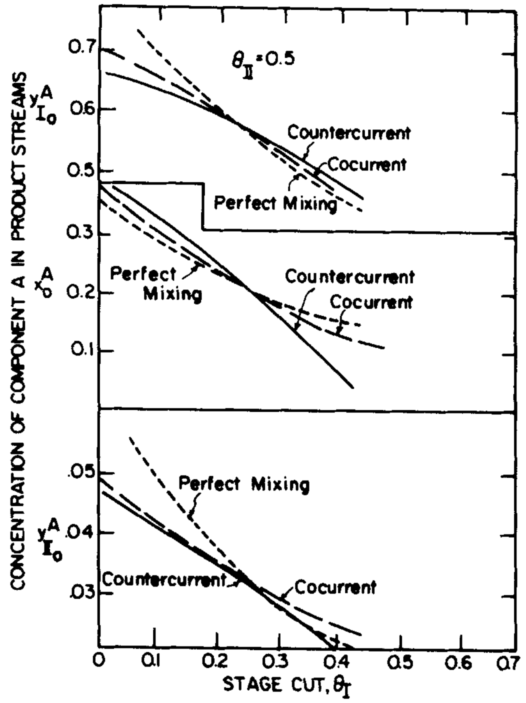

Figure 11. Separation of a binary gas mixture in a two-membrane permeator. Concentration of component A in product streams as a function of stage cut θ_I and flow pattern. θ_{II} = 0.5.

permeator depends on two stage cuts, θ_I and θ_{II}. Assuming "perfect-mixing" conditions, a study was made to determine how the separation of a hypothetical gas mixture of components A and B in such a permeator is affected by varying both θ_I and θ_{II}. Accordingly, the permeability coefficients for these components in membrane I were chosen arbitrarily as 5.0×10^{-8} and 0.5×10^{-8} $cm^3(STP) \cdot cm/(s \cdot cm^2 \cdot cm\ Hg)$, respectively. The corresponding permeability coefficients for the two components in membrane II were chosen as 0.5×10^{-8} and 5×10^{-8} $cm^3(STP) \cdot cm/(s \cdot cm^2 \cdot cm\ Hg)$. Hence, the ideal separation factors for the two membranes are $\alpha_I^* = 10$ and $\alpha_{II}^* = 0.10$, respectively. The feed flow rate was taken as 1×10^6 $cm^3(STP)/s$, and the thickness of each membrane was assumed to be 2.54×10^{-3} cm (1 mil). In addition, the pressure ratio across each membrane was selected as 5, with $p_{(A)} = 5 \times 10^5$ N/m^2 (380 cm Hg) and $p_{I(\ell)} = p_{II(\ell)} = 1 \times 10^5$ N/m^2 (76 cm Hg). The concentration of component A in the feed was specified to be 21%.

a. *Composition of product streams.* The quantitative results of these calculations are illustrated in Figure 6, where the concentration of component A in the three product streams from the two-membrane permeator is plotted vs. θ_I for different constant values of θ_{II}. The results for a single-membrane permeator using membrane I *only* is shown for comparison. In this instance, the single-membrane permeator can be visualized as having a zero stage cut for membrane II.

As can be seen from Figure 6, as the stage cut for membrane I increases, for a fixed θ_{II}, the concentration of component A in the permeate from membrane I decreases. This is similar to the behavior of the single-membrane permeator. The decrease in concentration of component A is the result of an increased flux of component B with increasing stage cut. Conversely, as the stage cut for membrane II increases, for a fixed θ_I, the concentration of component A in the permeate from membrane I also increases. This is due to the fact that, as θ_{II} increases, more of component B is allowed to permeate through membrane II. Consequently, the unpermeated product stream becomes enriched in component A.

Unlike the single-membrane permeator where the unpermeated stream is *always* less concentrated in the more rapidly permeating component (here component A) than the feed, under certain operating conditions ($\theta_I < \theta_{II}$) it is possible for the concentration of this component in the unpermeated product stream to be *higher* than in the feed. Such a behavior, which is illustrated in Figure 6, is predicted for cocurrent and countercurrent flow as well.

b. *Membrane area requirements.* The areas A_I and A_{II} of membranes I and II are plotted for "perfect-mixing" conditions in Figure 7 as a function of the corresponding stage cuts θ_I and θ_{II}. As is shown in the figure, A_I decreases as θ_{II} is increased at constant θ_I. This, again, can be attributed to the higher concentration of component A on the high pressure side and leading to a large concentration gradient (high driving force for separation) across membrane I. Similarly, as θ_I is increased, at constant θ_{II}, A_{II} decreases as a result of an increase in the concentration of component B in the unpermeated (high pressure) stream.

The membrane area requirement for a single-membrane permeator containing membrane I only is indicted by a dashed line and θ_{II} = 0.0. As illustrated in Figure 7, the area of membrane I in a two-membrane permeator is smaller than the corresponding area of a single-membrane permeator for all combinations of θ_I and θ_{II}. However, the membrane area requirement of a two-member permeator is the sum of A_I and A_{II}. As an example, for θ_I = 0.4, the membrane areas of a two-membrane permeator (θ_{II} = 0.5) and a single-membrane permeator are roughly 4.5×10^4 and $4.4 \times 10^4 m.^2$, respectively. Hence, the addition of a second type of membrane to a permeator module does not increase the membrane area of the separation process significantly.

c. *Separation factor.* An important quantity encountered in membrane separation processes is the stage separation factor, which is given for a single-membrane permeator by the relation:

$$\alpha = (y_o^A/1 - y_o^A)/(x_o^A/1 - x_o^A) \tag{31}$$

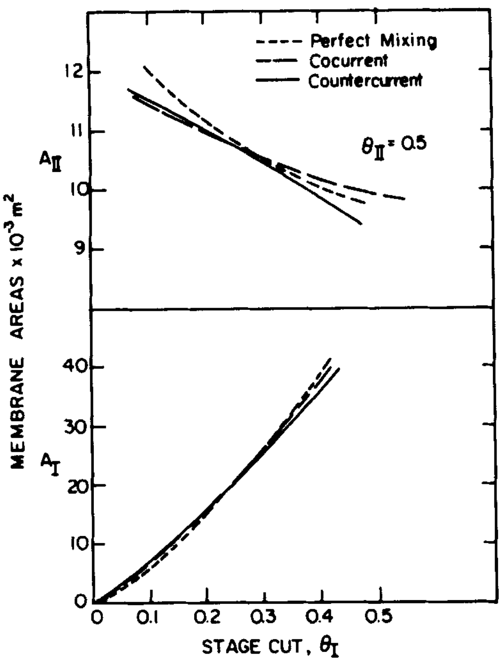

Figure 12. Separation of a binary gas mixture in a two-membrane permeator. Membrane areas A_I and A_{II} as a function of stage cut θ_I and flow pattern. θ_{II} = 0.5.

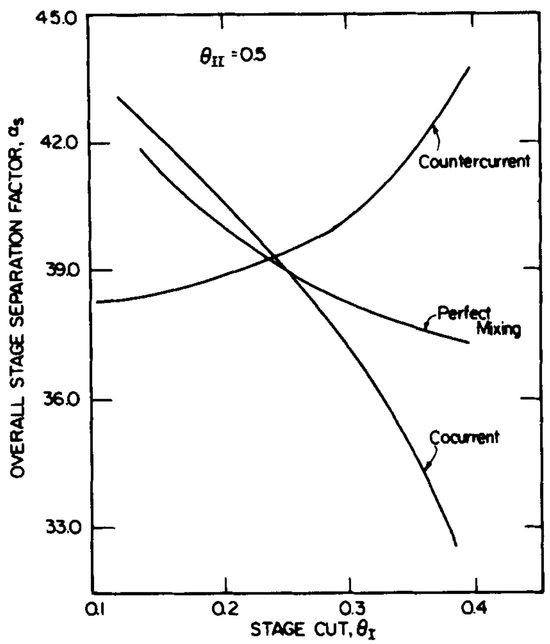

Figure 13. Separation of a binary gas mixture in a two-membrane permeator. Overall stage separation factor as a function of stage cut θ_I and flow pattern. θ_{II} = 0.5.

For a two-membrane permeator, a stage separation factor can be defined for each membrane as follows:

$$\alpha_I = (y^A_{Io}/1 - y^A_{Io})/x^A_o/1 - x^A_o) \tag{32}$$

$$\alpha_{II} = (y^A_{IIo}/1 - y^A_{IIo})/(x^A_o/1 - x^A_o) \tag{33}$$

Additionally, an *overall* stage separation factor can be defined (Ohno et al., 1977) as follows:

$$\alpha_s = \alpha_I/\alpha_{II} \tag{34}$$

A high separation (large value of α_s) is achieved when the maximum amount of component A is removed by membrane I (large value of α_I) and the maximum amount of component B is removed by membrane II (small value of α_{II}).

For a two-membrane permeator operating under "perfect-mixing" conditions, α_s is plotted as a function of the stage cuts θ_I and θ_{II} in Figure 8. As can be seen from this figure, the overall stage separation factor increases with an increase in stage cut θ_{II}, while it decreases as θ_I is increased. No comparison is made between the separation factor of a two-membrane permeator, α_s, and that of a single-membrane permeator, α, due to differences in their definition.

2. *Comparison of Flow Patterns.* In Figures 9–11 is plotted the concentration of component A in the permeate from membrane I as a function of θ_I for each flow pattern investigated (i.e., "perfect mixing," cocurrent, and countercurrent flow). The stage cut θ_{II} for membrane II is constant in each figure. As can be discerned from Figures 9–11, there exists a regime of stage cuts for which "perfect mixing" is the most favorable flow pattern because it yields the highest value of y^A_{IIo}, the mole fraction of component A in the permeate from membrane I. (This is contrary to the behavior of the single-membrane permeator.) This regime corresponds to operating conditions in which the stage cut for membrane I is smaller than that for membrane II ($\theta_I < \theta_{II}$). Under such conditions, the unpermeated (high-pressure) stream is gradually enriched in component A, as indicated in Figure 6, rather than depleted in this component as is the case in a single-membrane permeator. In Figures 9–11, all three flow patterns yield the same value of y^A_{IIo} when the feed and the unpermeated stream have the same composition.

Typical plots of the membrane areas and overall stage separation factor are presented in Figures 12 and 13 for θ_{II} = 0.5. In Figure 12, for $\theta_I < \theta_{II}$, the minimum area for membrane I is achieved with "perfect mixing." By contrast, in Figure 13, "perfect-mixing" is never the "best" flow pattern, i.e., the flow pattern with the highest value of α_s.

The above results indicate that the addition of a second type of membrane to a permeator module can increase the concentration of the desired component in one of the product stream, and hence the separation efficiency, without increasing the membrane area requirement of the permeator.

Multimembrane permeation systems do not necessarily require that the different types of membranes be housed in the same permeator module. Each membrane can be confined to its own permeator, where countercurrent flow is *always* the most favorable flow pattern (Weller and Steiner, 1950a,b; Stern and Walawender, 1967, 1972; Blaisdell and Kammermeyer, 1973; Hwang and Kammermeyer, 1975); the different permeators can be connected either in series or in parallel. Preliminary calculations for two-membrane permeation systems indicate that the highest separation of a binary mixture by means of two different types of membranes is achieved when both types of membrane are housed in the same permeator module (Stern et al., 1983).

Finally, it should be noted that the properties of two-membrane permeators have been studied also by Sengupta and Sirkar (1983), who examined the separation of ternary mixtures in such devices. In these cases, the component of the mixture that exhibits the lowest rate of permeation through both membranes will concentrate in the unpermeated high-pressure stream. This will necessarily affect the extent of separation of the other two components. However, Sengupta and Sirkar reached the same general conclusions on the operation of two-membrane permeators as obtained in the present study.

ACKNOWLEDGMENT

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NOTATION

A = membrane area
D = hollow fiber diameter
L = local high-pressure molar flow rate
L_{I} = local molar flow rate on low-pressure side of membrane I
L_{II} = local molar flow rate on low-pressure side of membrane II
$L_{i(h)}$ = high-pressure molar flow rate at the stage inlet
$L_{o(h)}$ = high-pressure molar flow rate at the stage outlet
$L_{o(\ell)}$ = low-pressure molar flow rate at the stage outlet
N = number of hollow fibers in permeator module
$\bar{P}^A$ = mean permeability coefficient for component A
$\bar{P}^B$ = mean permeability coefficient for component B
$p_{(h)}$ = total pressure (absolute) on high-pressure side of the membrane
$p_{(\ell)}$ = total pressure (absolute) on low-pressure side of the membrane
r = pressure ratio $p_{(h)}/p_{(\ell)}$
R = membrane area ratio $A_{\mathrm{I}}/A_{\mathrm{II}}$
x^a = local high-pressure mole fraction of component A
x^b = local high-pressure mole fraction of component B; $1 - x^A$ for binary system
x_i^A = high-pressure mole fraction of component A at stage inlet
x_o^A = high-pressure mole fraction of component A at stage outlet
y^A = local low-pressure mole fraction of component A
y^B = local low-pressure mole fraction of component B; $1 - y^A$ for binary systems
y_i^A = low-pressure mole fraction of component A at the stage inlet
y_o^A = low-pressure mole fraction of component A at the stage outlet

Greek Letters

α = stage separation factor, $(y_o^A/1 - y_o^A)/(x_o^A/1 - x_o^A)$
α^* = ideal separation factor, $\bar{P}^A/\bar{P}^B$
α_s = overall stage separation factor, $\alpha_{\mathrm{I}}/\alpha_{\mathrm{II}}$
δ = membrane thickness
θ = stage cut, $L_{o(\ell)}/L_{i(h)}$

Subscripts

$h, (h)$ = high pressure
i = inlet
I = membrane I
II = membrane II
$\ell, (\ell)$ = low pressure
o = outlet

Superscripts

A,B = component

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