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Analysis of Membrane Separation Parameters

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Summary

This study is concerned with the separation of gas mixtures by selective permeation through nonporous polymeric membranes, a technique that has made considerable progress in recent years. First, several theoretical methods for calculating the separation achievable in a single permeation stage are reviewed and their advantages and limitations are discussed. The methods under consideration assume two idealized flow regimes inside the stage, which are characterized by (a) perfect mixing on both sides of the membrane and (b) cross-flow with no mixing on either side of the membrane. Computer programs for the numerical evaluation of these methods are presented. Second, the effects of several important process variables on the single-stage separation and membrane area requirements are outlined in a parametric study, with special reference to the separation of oxygen from air. The variables include (a) the ratio of pressures on the two sides of the membrane, (b) the pressure level at constant pressure ratio, (c) the fraction of feed permeated (the stage "cut"), and (d) the ideal separation factor. The practical implications of the results are also discussed.

INTRODUCTION

The selective permeation of gases through nonporous polymeric membranes is a potentially effective separation technique that has attracted much attention since the early 1950s. This technique has made considerable progress in recent years, as witnessed by the development of more permeable and selective membranes, as well as of efficient permeation equipment for large-scale applications. Although much of the work in this field is being done by private industry and, consequently, is of a propriety nature, several important gas-permeation processes have been discussed in the literature. These processes include the separation of oxygen from air (*1–8*), the recovery of helium from natural gas (*1–3, 5–11*), the separation of hydrogen from industrial gas mixtures (*2–4, 6, 8, 12–14*), and the control of carbon dioxide in sealed environments (*6*). The study of selective permeation is generally motivated by the ever-present economic necessity of developing more competitive separation methods. The investigation of carbon dioxide control is perhaps an exception, since it has been aimed towards a reduction in the weight and size of separation equipment used in aerospace missions.

In order to assess the potential usefulness of a gas-permeation process, whether in terms of process economics or hardware requirements, it is important to determine the number of stages and the membrane area necessary to perform the desired separation. For any specific gas mixture and membrane system, the degree of separation achievable in a single permeation stage will depend on the operating variables. The latter include the pressures on the two sides of the membrane; the temperature; the fraction of the feed allowed to permeate, i.e., the stage "cut"; and the flow pattern of the gas on both sides of the membrane. Theoretical studies of gas separation by selective permeation in a single stage have been made by several investigators. One of the objectives of the present paper is to review and compare some of the analytical methods that have been proposed for this purpose, and to discuss their advantages and limitations. Computer programs for the numerical evaluation of these methods are also described.

Another objective is to present the results of a parametric study of the effect of the above operating variables on the extent of separation and the membrane area requirements. The study was made with reference to the single-stage separation of oxygen from air by means of hypothetical membranes with varying permeability properties. The membrane-area requirements are of particular interest from an economic viewpoint because they determine a large fraction of the investment costs of a large permeation plant. Recent studies have indicated that these costs may constitute as much as 95% of the total costs of a gas-permeation process, based on the membranes available at present (*6, 9*). Finally, the practical implications of this study are discussed in some detail.

REVIEW OF ANALYTICAL STUDIES

The first analytical study on the separation of gas mixtures in a single permeation stage was made by Weller (*2, 3*). He considered two limiting flow regimes inside the stage: (a) when perfect mixing occurs on both sides of the membrane, and (b) when there is no mixing on either side of the membrane. Weller's theory was limited to the separation of binary mixtures, but the perfect mixing case was extended by Huckins and Kammermeyer (*15*, *16*) and by Brubaker and Kammermeyer (*17*) to ternary and quaternary mixtures. The extension of Weller's second case, of no mixing, to multicomponent mixtures is complicated from an analytical standpoint. A simpler iterative method for both cases, which is suitable for computer calculations, has been described by Stern et al. (*9*). A different formulation for the separation of binary mixtures, under conditions where no mixing occurs on either side of the membrane, has been reported also by Naylor and Backer (*18*) for porous barriers; however, as shown below, their equations apply equally well to permeation through nonporous polymeric membranes. The results obtained by these investigators are reviewed and discussed below.

Perfect-Mixing Case

The Weller Method. (*2*, *3*) Reference is made to Fig. 1, which is a schematic diagram of a permeation stage. As indicated, the stage is divided into two sections by a nonporous membrane. A binary mixture of components A and B is introduced into one section of the stage at a total pressure p_h and a molar flow rate $L_{i(h)}$, where the subscript i

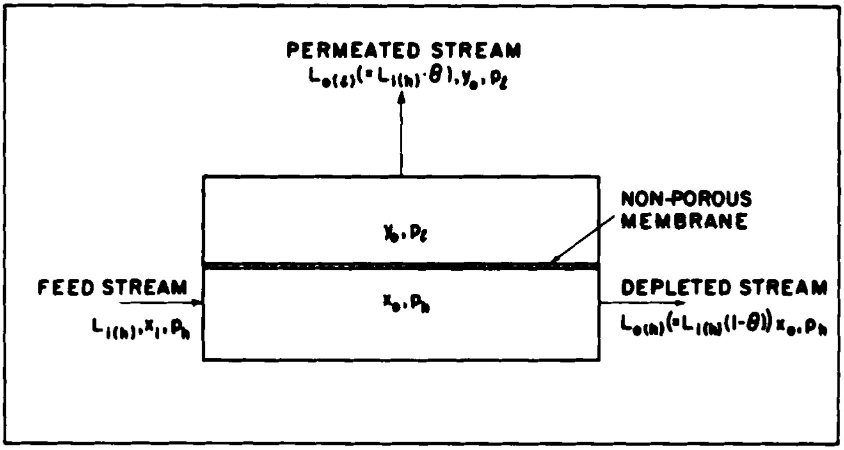

FIG. 1. Diagram of a single permeation stage with perfect mixing on both sides of the membrane.

stands for "inlet" and the subscript h indicates the high-pressure side of the membrane, or stage; the mole-fraction of the more permeable component (assumed to be A) in the feed stream is x_i^A. The pressure p_h is held constant throughout this section of the stage. A specified fraction of the feed, θ, is allowed to permeate through the membrane into the second section of the stage, which is maintained at a lower pressure, p_ℓ; θ is sometimes designated as the stage "cut." As a result, the feed stream is separated into a permeated stream enriched in component A and an unpermeated stream depleted in this component. When leaving the stage, the molar flow rates of these streams are $L_{o(\ell)}$ and $L_{o(h)}$, respectively, and the corresponding mole-fractions of A are y_o^A and x_o^A; the subscript o stands for "outlet" and ℓ designates the low-pressure side of the membrane or stage. The mole fraction y_o^A has been called the "enrichment."

In one of the limiting cases studied, Weller assumed that the rate of mixing on the high-pressure side is so rapid, as compared with the flow rate, that the unpermeated gas has *at all points in the stage* the same composition as the unpermeated gas stream leaving the stage. The same assumption is made for the low-pressure side of the stage. The rates of permeation are further assumed to obey Fick's law, which takes the following forms for the two components under steady-state conditions:

$$y_o^A L_{o(\ell)} = P^A \left(\frac{\mathcal{A}}{t}\right)(p_h x_o^A - p_\ell y_o^A) \tag{1}$$

and

$$(1 - y_o^A)L_{o(\ell)} = P^B \left(\frac{\mathcal{A}}{t}\right)[p_h(1 - x_o^A) - p_\ell(1 - y_o^A)] \tag{2}$$

where $\mathcal{A}$ and t are the area and thickness of the membrane, respectively, and P^A and P^B are the permeability coefficients for the pure components A and B. The material balances for the stage are

$$L_{i(h)} = L_{o(h)} + L_{o(\ell)} \tag{3}$$

and

$$L_{i(h)}x_i^A = L_{o(h)}x_o^A + L_{o(\ell)}y_o^A \tag{4}$$

Let also

$$\alpha^* = \frac{P^A}{P^B} \tag{5}$$

$$\beta = \frac{L_{o(\ell)}}{(\mathcal{A}/t)P^A} \tag{6}$$

and

$$\gamma = \frac{L_{o(h)}}{L_{i(h)}} \tag{7}$$

where α^* is an ideal local or point separation factor, which is discussed in the Appendix. Equations (1) to (7) yield, by means of appropriate algebraic manipulations, the following expressions for y_o^A, x_o^A, and x_i^A, the mole-fractions of the more permeable component in the permeated, unpermeated, and feed streams, respectively:

$$y_o^A = \frac{\alpha^* - (p_h - p_l)/\beta}{\alpha^* - 1} \tag{8}$$

$$x_o^A = \left(\frac{\beta + p_l}{p_h}\right)\left[\frac{\alpha^* - (p_h - p_l)/\beta}{\alpha^* - 1}\right] = \frac{(\beta + p_l)y_o^A}{p_h} \tag{9}$$

$$x_i^A = \left[(1 - \gamma) + \frac{\gamma(\beta + p_l)}{p_h}\right]\left[\frac{\alpha^* - (p_h - p_l)/\beta}{\alpha^* - 1}\right] = (1 - \gamma)y_o^A + \gamma x_o^A \tag{10}$$

Equation (10) can also be written in terms of the stage cut θ, since

$$\theta = \frac{L_{o(l)}}{L_{i(h)}} \tag{11}$$

and

$$\gamma = 1 - \theta \tag{12}$$

Generally, the values of P^A and P^B, γ or θ, p_h and p_l, x_i^A, and $L_{i(h)}$ are known. Then, β is obtained from Eq. (10), which yields, in turn, the values of y_o^A and x_o^A from Eqs. (8) and (9). Finally, the membrane area $\mathcal{A}$ is calculated from Eq. (6) for a specified thickness t.

The Huckins and Kammermeyer Method. (*15*, *16*) The above treatment has been modified slightly by Huckins and Kammermeyer. By dividing Eqs. (1) and (2), we obtain

$$\frac{y_o^A}{1 - y_o^A} = \alpha^* \frac{(p_h x_o^A - p_l y_o^A)}{p_h(1 - x_o^A) - p_l(1 - y_o^A)} \qquad p_h > p_l \tag{13}$$

The value of y_o^A is calculated from this quadratic equation, the solution of which is

$$y_o^A = \frac{(\alpha^* - 1)(r x_o^A + 1) + r \pm \{[(\alpha^* - 1)(r x_o^A + 1) + r]^2 - 4\alpha^*(\alpha^* - 1) r x_o^A\}^{1/2}}{2(\alpha^* - 1)} \tag{14}$$

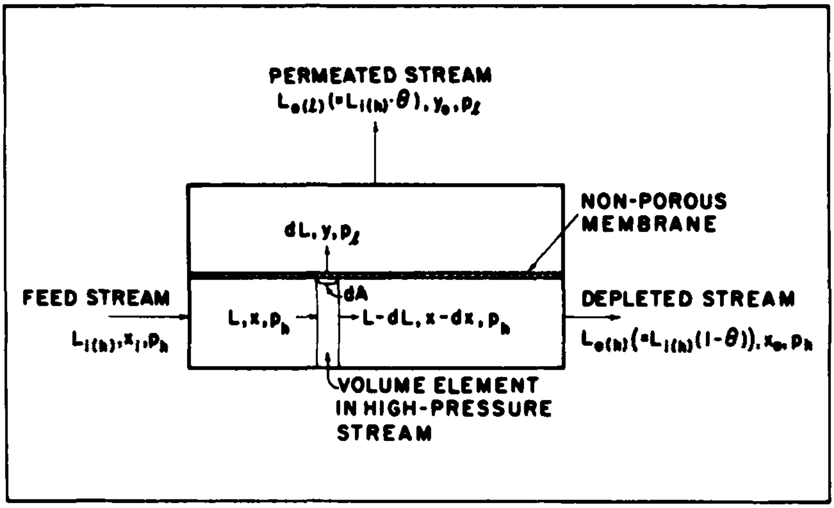

FIG. 2. Diagram of a single permeation stage for cross-flow and with no mixing on either side of the membrane.

where

$$r = \frac{p_h}{p_l} \tag{15}$$

The calculation requires that x_o^A, the mole-fraction of the more permeable component in the unpermeated stream, be known, in addition to α^* and r. Since x_o^A is usually not known, it must be found from the material-balance equation (4), after substituting Eq. (14) for y_o^A. This procedure is somewhat cumbersome.

The Iteration Method. (*9*) This method is particularly useful for multicomponent mixtures and consequently will be discussed relative to a ternary mixture of components A, B, and C. Referring to Fig. 1, the problem is to determine the unknown quantities

$$y_o^A,\ y_o^B,\ y_o^C;\quad x_o^A,\ x_o^B,\ x_o^C;\quad L_{o(l)} \text{ or } L_{o(h)};\quad \text{and } \mathfrak{A}$$

knowing the values of

$$x_i^A,\ x_i^B, \text{ or } x_i^C;\quad L_{i(h)};\quad \theta;\quad p_h \text{ and } p_l;\quad P^A,\ P^B,\ P^C;\quad \text{and } l$$

The eight unknowns can be found by solving a set of eight simultaneous equations; these include three continuity equations similar to Eq. (1) for the components A, B, and C, three material-balance equations similar to Eq. (4), and the two conditions

$$\sum_n x_i^n = 1 \tag{16}$$

and

$$\sum_n y_o^n = 1 \tag{17}$$

where n designates the components.

The above relations yield the following expression for the membrane area:

$$\mathfrak{a} = \frac{L_{o(t)} y_o^A t}{P^A[(p_h/1 - \theta)(x_i^A - \theta y_o^A) - p_l y_o^A]} \tag{18}$$

The mole-fractions y_o^B and y_o^C in the permeate stream are given by

$$y_o^B = \frac{(p_h x_i^B/1 - \theta)}{(L_{o(t)} t/P^B \mathfrak{a}) + (\theta/1 - \theta) p_h + p_l} \tag{19}$$

and

$$y_o^C = \frac{(p_h x_i^C/1 - \theta)}{(L_{o(t)} t/P^C \mathfrak{a}) + (\theta/1 - \theta) p_h + p_l} \tag{20}$$

The following procedure is used to solve these equations:

(a) A value is assumed for y_o^A.

(b) The membrane area is calculated from Eq. (18), and $L_{o(h)}$ or $L_{o(t)}$ is calculated from the material-balance equation (3).

(c) Next, y_o^B and y_o^C are calculated from Eqs. (19) and (20), respectively.

(d) $\Sigma_n\, y_o^n$ is determined, and steps (a) to (c) are repeated until $\Sigma_n\, y_o^n = 1$.

(e) x_o^A, x_o^B, and x_o^C are calculated from the material balance equations.

It should be noted that the three methods discussed above differ only in the procedure used to solve the same set of continuity and conservation equations.

No-Mixing Case

The Weller Method. (*2*, *3*) In this case, the flow pattern in the stage can be designated as "cross flow": the gas on the high-pressure side of the stage flows parallel to the membrane, while the permeate flows perpendicular to, and away from, the membrane. Weller assumed that no mixing takes place on the high-pressure side, as would be expected for undisturbed laminar or plug flow. He also assumed that no mixing occurs on the low-pressure side: the permeate composition *at any point* near the membrane is then determined by the relative rates of permeation of the feed components at that point. The latter assumption implies, as mentioned by Breuer and Kammermeyer (*19*), that the membrane is situated sufficiently far away from the permeate stream leaving the stage so that the gas composition next to the membrane is not affected by this stream. Should high turbulence occur on both sides of the membrane, this case would reduce to perfect mixing conditions.

The analytical procedure in the no-mixing case is considerably more complicated than for perfect mixing conditions, as shown with reference to Fig. 2. The *local* permeation rates of the components A and B of a binary mixture, at any point or cross section of the stage, can be expressed at steady state, in terms of Fick's law, as follows:

$$y^{\mathrm{A}}\,dL = P^{\mathrm{A}}\left(\frac{d\mathcal{A}}{t}\right)(p_h x^{\mathrm{A}} - p_\ell y^{\mathrm{A}}) \tag{21}$$

and

$$(1 - y^{\mathrm{A}})\,dL = P^{\mathrm{B}}\left(\frac{d\mathcal{A}}{t}\right)[p_h(1 - x^{\mathrm{A}}) - p_\ell(1 - y^{\mathrm{A}})] \tag{22}$$

where x^{A} and y^{A} are the local compositions (in mole-fractions) of component A on the high- and low-pressure sides of the membrane, respectively; dL is the total molar flux through an element of membrane area $d\mathcal{A}$; and the other symbols have the same meaning as before.

The ratio of Eqs. (21) and (22) is

$$f = \alpha^* \left[\frac{p_h(i/i + 1) - p_\ell(f/f + 1)}{p_h(1/i + 1) - p_\ell(1/f + 1)}\right] \tag{23}$$

where

$$f = \frac{y^{\mathrm{A}}}{1 - y^{\mathrm{A}}} \tag{24}$$

$$i = \frac{x^{\mathrm{A}}}{1 - x^{\mathrm{A}}} \tag{25}$$

and

$$\alpha^* = \frac{P^{\mathrm{A}}}{P^{\mathrm{B}}} \tag{5}$$

The solution of this quadratic equation is

$$f = (Di - F) + (D^2i^2 + 2Ei + F^2)^{1/2} \tag{26}$$

where

$$D = \frac{1}{2}\left[(1 - \alpha^*)\frac{p_\ell}{p_h} + \alpha^*\right] \tag{27}$$

$$E = \frac{\alpha^*}{2} - DF \tag{28}$$

and

$$F = -\frac{1}{2}\left[(1 - \alpha^*)\frac{p_\ell}{p_h} - 1\right] \tag{29}$$

Separation of variables is obtained by observing that

$$f = \frac{dL^A}{dL^B} \tag{30}$$

and

$$i = \frac{L^A}{L^B} \tag{31}$$

where

$$dL^A = y^A \, dL \tag{32}$$

and

$$dL^B = (1 - y^A) \, dL \tag{33}$$

and L^A and L^B represent the molar flow rate of components A and B at any point on the high-pressure side of the stage ($L = L^A + L^B$). Equation (26) then yields the expression

$$\frac{dL^B}{L^B} = \frac{di}{f - i} = \frac{di}{(D - 1)i - F + (D^2i^2 + 2Ei + F^2)^{1/2}} \tag{34}$$

It is now convenient to change to a new variable u, which is defined by

$$u \equiv -Di + (D^2i^2 + 2Ei + F^2)^{1/2} \tag{35}$$

Substitution of u in Eq. (34) yields

$$\frac{dL^B}{L^B} = -\frac{(Du^2 - 2Eu + DF^2)}{(Du - E)(u - F)(u + F - \alpha^*)}\,du \tag{36}$$

By integrating the above equation from the stage inlet across the stage, Weller obtained the following relation between $L^{\mathrm{B}}_{\mathrm{i(h)}}$ and L^{B}, where $L^{\mathrm{B}}_{\mathrm{i(h)}}$ is the molar flow rate of component B in the feed stream:

$$\ln\frac{L^{\mathrm{B}}}{L^{\mathrm{B}}_{\mathrm{i(h)}}} = R\ln\left(\frac{u_{\mathrm{i}} - (E/D)}{u - (E/D)}\right) + S\ln\left(\frac{u_{\mathrm{i}} - \alpha^* + F}{u - \alpha^* + F}\right) + T\ln\left(\frac{u_{\mathrm{i}} - F}{u - F}\right) \tag{37}$$

where

$$R = \frac{1}{2D - 1} \tag{38}$$

$$S = \frac{\alpha^*(D - 1) + F}{(2D - 1)[(\alpha^*/2) - F]} \tag{39}$$

and

$$T = \frac{1}{1 - D - (E/F)} \tag{40}$$

The quantities D, E, F and R, S, T depend only on the pressure ratio r and the ideal separation factor α^*, i.e., on P^{A} and P^{B}.

The following computational procedure may be followed. A value is first assumed for i_{o} $(= L^{\mathrm{A}}_{\mathrm{o(h)}}/L^{\mathrm{B}}_{\mathrm{o(h)}})$; this determines u_{o}, the value of u at the stage outlet. The feed rate and composition define i_{i} $(= L^{\mathrm{A}}_{\mathrm{i(h)}}/L^{\mathrm{B}}_{\mathrm{i(h)}})$, and hence also u_{i}, the value of u at the stage inlet. Then, using the above u_{o} and u_{i}, and for a given pressure ratio r and separation factor α^*, the value of $L^{\mathrm{B}}_{\mathrm{o(h)}}$ can be calculated by means of Eq. (37) as a function of $L^{\mathrm{B}}_{\mathrm{i(h)}}$. The corresponding $L^{\mathrm{A}}_{\mathrm{o(h)}}$ is then obtained by virtue of the relation $L^{\mathrm{A}}_{\mathrm{o(h)}} = i_{\mathrm{o}}L^{\mathrm{B}}_{\mathrm{o(h)}}$. The composition of the unpermeated gas stream leaving the stage is thus established. The composition of the permeate is calculated from $L^{\mathrm{A}}_{\mathrm{i(h)}}$, $L^{\mathrm{B}}_{\mathrm{i(h)}}$, $L^{\mathrm{A}}_{\mathrm{o(h)}}$, and $L^{\mathrm{B}}_{\mathrm{o(h)}}$; for example, the mole-fraction of component A in the permeate stream leaving the stage, $y_{\mathrm{o}}{}^{\mathrm{A}}$, is given by

$$y_{\mathrm{o}}{}^{\mathrm{A}} = \frac{L^{\mathrm{A}}_{\mathrm{o}(l)}}{L_{\mathrm{o}(l)}} = \frac{L^{\mathrm{A}}_{\mathrm{i(h)}} - L^{\mathrm{A}}_{\mathrm{o(h)}}}{L_{\mathrm{i(h)}} - L_{\mathrm{o(h)}}} = \frac{L^{\mathrm{A}}_{\mathrm{i(h)}} - L^{\mathrm{A}}_{\mathrm{o(h)}}}{(L^{\mathrm{A}}_{\mathrm{i(h)}} + L^{\mathrm{B}}_{\mathrm{i(h)}}) - (L^{\mathrm{A}}_{\mathrm{o(h)}} + L^{\mathrm{B}}_{\mathrm{o(h)}})} \tag{41}$$

Obviously $y_{\mathrm{o}}{}^{\mathrm{A}}$ is an average composition. The stage cut θ is determined from

$$\theta = \frac{L_{\mathrm{o}(l)}}{L_{\mathrm{i(h)}}} = \frac{L_{\mathrm{i(h)}} - L_{\mathrm{o(h)}}}{L_{\mathrm{i(h)}}} = \frac{(L^{\mathrm{A}}_{\mathrm{i(h)}} + L^{\mathrm{B}}_{\mathrm{i(h)}}) - (L^{\mathrm{A}}_{\mathrm{o(h)}} + L^{\mathrm{B}}_{\mathrm{o(h)}})}{(L^{\mathrm{A}}_{\mathrm{i(h)}} + L^{\mathrm{B}}_{\mathrm{i(h)}})} \tag{42}$$

Thus the value of $y_{\mathrm{o}}{}^{\mathrm{A}}$ can be obtained as a function of θ.

The required membrane area, $\mathcal{A}$, is calculated from the expression

$$\mathcal{A} = -\frac{t}{P^{\mathrm{B}}} \int_{i_i}^{i_o} \frac{L^{\mathrm{B}}\, di}{(f - i)[p_h(1/1 + i) - p_l(1/1 + f)]} \tag{43}$$

which is obtained from Eq. (22) in conjunction with Eqs. (24) and (25), and where L^{B} is given by Eq. (37). The integral can be evaluated numerically, with the aid of a digital computer, or graphically.

The Naylor and Backer Method. (*18*) This method was originally developed for the separation of binary mixtures by gaseous diffusion across a *porous* barrier, when the separation factor is large. If the gas flow through the barrier is in the molecular, or Knudsen, regime, the molar flow rates of the two components of the mixture across any element of barrier area are given (approximately) by the following expressions:

$$y^{\mathrm{A}}\, dL = Q^{\mathrm{A}} \left(\frac{d\mathcal{A}}{t}\right) (p_h x^{\mathrm{A}} - p_l y^{\mathrm{A}}) \tag{44}$$

and

$$(1 - y^{\mathrm{A}})\, dL = Q^{\mathrm{B}} \left(\frac{d\mathcal{A}}{t}\right) [p_h(1 - x^{\mathrm{A}}) - p_l(1 - y^{\mathrm{A}})] \tag{45}$$

where

$$Q^{\mathrm{A,B}} = \frac{4d}{3}\left(\frac{2 - \mathscr{f}}{\mathscr{f}}\right) \lambda \left(\frac{1}{2\pi M^{\mathrm{A,B}} \mathcal{R} \mathcal{T}}\right)^{1/2} \tag{46}$$

In the last expression, $Q^{\mathrm{A,B}}$ is a barrier permeability coefficient for components A or B; d is the diameter of the pores in the barrier, which are assumed to be straight, circular capillaries; $\mathscr{f}$ is the fraction of molecules that strike the pore wall and are emitted with random velocity distribution; λ is the fraction of the barrier open to gas flow; $M^{\mathrm{A,B}}$ is the molecular weight of components A or B; $\mathcal{R}$ is the universal gas constant; and $\mathcal{T}$ is the absolute temperature.

Equations (44) and (45), which were used by Naylor and Backer, are entirely similar to Eqs. (21) and (22), except that the barrier permeabilities Q^{A} and Q^{B} are substituted for the membrane permeability coefficients P^{A} and P^{B}. The former can be calculated by means of Eq. (46), while the latter must be determined experimentally. However, both sets of permeability coefficients depend only on the gas–membrane or gas–barrier systems under consideration and on the temperature. Hence, the treatment of Naylor and Backer is applicable also to the separation of gas mixtures by permeation through nonporous polymeric membranes, provided that Q^{A} and Q^{B} are replaced by P^{A} and P^{B}.

Naylor and Backer, like Weller, assumed cross-flow of high- and low-pressure streams in the stage, and no mixing on either side of the membrane. Their method is presented below in some detail, for comparison with the analytical approach taken by Weller in this case. They first calculated a local rate of permeation of component A through an element of membrane area; this rate was obtained from a material balance around a differential volume element in the high-pressure stream, such as shown in Fig. 2. The material balance is given below, after rearrangement of terms:

$$\frac{dL}{L} = \frac{dx^{\mathrm{A}}}{y^{\mathrm{A}} - x^{\mathrm{A}}} = \left[\frac{1 + \epsilon x^{\mathrm{A}}}{x^{\mathrm{A}}\epsilon(1 - x^{\mathrm{A}})}\right] dx^{\mathrm{A}} \tag{47}$$

where ϵ $(= \alpha - 1)$ is the actual local or point enrichment factor (see Appendix). The above balance equation is similar, incidentally, with that for Rayleigh (batch) distillation.

Under the assumption of constant enrichment (or separation) factor, Eq. (47) is integrated from the volume element to the stage outlet in order to yield an expression for L:

$$L = L_{\mathrm{i(h)}}(1 - \theta)\left[\left(\frac{x^{\mathrm{A}}}{x_{\mathrm{o}}^{\mathrm{A}}}\right)^{1/\epsilon}\left(\frac{1 - x_{\mathrm{o}}^{\mathrm{A}}}{1 - x^{\mathrm{A}}}\right)^{\sigma}\right] \tag{48}$$

where L is the total molar flow rate at any point or cross section on the high-pressure side of the stage, and $\sigma = (\epsilon + 1)/\epsilon$. The average mole-fraction of A in the permeate stream, $y_{\mathrm{o}}^{\mathrm{A}}$, is then obtained from the relation

$$y_{\mathrm{o}}^{\mathrm{A}} = \frac{\int_{x_{\mathrm{i}}^{\mathrm{A}}}^{x_{\mathrm{o}}^{\mathrm{A}}} y\, dL}{\int_{x_{\mathrm{i}}^{\mathrm{A}}}^{x_{\mathrm{o}}^{\mathrm{A}}} dL} = -\frac{1}{\theta L_{\mathrm{i(h)}}}\int_{x_{\mathrm{i}}^{\mathrm{A}}}^{x_{\mathrm{o}}^{\mathrm{A}}} y^{\mathrm{A}}\, dL \tag{49}$$

The integrand on the right-hand side of Eq. (49) is obtained by multiplying the relation

$$y^{\mathrm{A}} = \frac{x^{\mathrm{A}}(1 + \epsilon)}{1 + \epsilon x^{\mathrm{A}}} \tag{50}$$

from the definition of the enrichment factor [see Appendix, Equation (f)] with Eqs. (47) and (48):

$$y_{\mathrm{o}}^{\mathrm{A}} = -\sigma\left(\frac{1 - \theta}{\theta}\right)\frac{(1 - x_{\mathrm{o}}^{\mathrm{A}})^{\sigma}}{(x_{\mathrm{o}}^{\mathrm{A}})^{1/\epsilon}}\int_{x_{\mathrm{i}}^{\mathrm{A}}}^{x_{\mathrm{o}}^{\mathrm{A}}}\frac{(x^{\mathrm{A}})^{1/\epsilon}}{(1 - x^{\mathrm{A}})^{\sigma+1}}\, dx^{\mathrm{A}} \tag{51}$$

Integration of Eq. (51) yields

$$y_{\mathrm{o}}^{\mathrm{A}} = (x_{\mathrm{o}}^{\mathrm{A}})^{-1/\epsilon}\left(\frac{1 - \theta}{\theta}\right)\left[(1 - x_{\mathrm{o}}^{\mathrm{A}})^{\sigma}\left(\frac{x_{\mathrm{i}}^{\mathrm{A}}}{1 - x_{\mathrm{i}}^{\mathrm{A}}}\right)^{\sigma} - (x_{\mathrm{o}}^{\mathrm{A}})^{\sigma}\right] \tag{52}$$

Finally, x_i^A or x_o^A can be eliminated from Eq. (51) by means of a material balance around the stage:

$$x_i^A = (1 - \theta)x_o^A + \theta y_o^A \tag{53}$$

For example, substituting for x_i^A yields

$$y_o^A = (x_o^A)^{-1/\epsilon}\left(\frac{1-\theta}{\theta}\right) \times \left\{(1 - x_o^A)^\sigma \left[\frac{(1-\theta)x_o^A + \theta y_o^A}{1 - [(1-6)x_o^A + \theta y_o^A]}\right]^\sigma - (x_o^A)^\sigma\right\} \tag{54}$$

where y_o^A is expressed in terms of x_o^A, θ, and the actual separation factor α. As shown in the Appendix, α depends on α^*, the pressure ratio r, and the composition x^A. However, the dependence on x^A is assumed to be negligible for any one stage, and a value of α corresponding to x_0^A may be used for conservative estimates. Naylor and Backer have pointed out that Eq. (54) is divergent for the purpose of iteration.

The paper of Naylor and Backer does not include determination of membrane or barrier area, but this can be obtained from Eq. (21) for the molar flux of one of the components across the element of area. Rearrangement and integration of Eq. (21) yields

$$\mathcal{A} = \int_{x_o^A}^{x_i^A} \frac{t y^A\,dL}{P^A(p_h x^A - p_l y^A)} \tag{55}$$

where $y^A\,dL$ is expressed as a function of x^A by the product of Eqs. (47), (48), and (50), and y^A is given by Eq. (50). The integral can be evaluated numerically.

The Iteration Method. (*9*) The application of this method to the no-mixing case is straightforward. It is assumed that the stage is divided in a large number of hypothetical sections, with the assumption of perfect mixing still holding for each individual section. A small incremental value is then taken for the molar flow rate $L_{o(l)}$, and the values of $L_{o(h)}$, $\mathcal{A}$, y_o^A, y_o^B, y_o^C, x_o^A, x_o^B, and x_o^C are computed as described earlier, in the section on the iteration method. The unpermeated gas stream from the first section is assumed to become the feed to the second section, and the calculation is repeated until the desired degree of removal of the more permeable component from the feed is achieved.

COMPUTER PROGRAMS

All computations in this study were performed with the aid of the General Electric Computer Time-Sharing System. Programs were written in the BASIC language for five of the analytical methods discussed previously; these programs are described below:

Program 1-PM

The first program employed the Weller method for the case of perfect mixing. As mentioned previously, specification of x_i^A, θ, p_h, p_l, P^A, P^B, $L_{i(h)}$, and t allows a value of β to be calculated from Eq. (10), using the positive root of the quadratic in β. With this result, y_o^A and x_o^A are computed from Eqs. (8) and (9), respectively, and the membrane area is determined from Eq. (6); the value of $L_{o(l)}$ appearing in the latter is obtained from Eq. (11).

Program 2-PM

The second program employed the iteration method for the case of perfect mixing. The pertinent equations for the separation of a binary mixture are

$$\alpha = \frac{L_{o(l)} y_o^A t}{P^A[(p_h/1 - \theta)(x_i^A - \theta y_o^A) - p_l y_o^A]} \tag{18}$$

$$x_o^A = \frac{1}{1 - \theta}(x_i^A - \theta y_o^A) \tag{53}$$

$$y_o^B = \frac{(p_h x_i^B/1 - \theta)}{(L_{o(l)} t/P^B \alpha) + (\theta/1 - \theta)p_h + p_l} \tag{20}$$

$$x_o^A + x_o^B = 1 \tag{56}$$

$$(y_o^A + y_o^B) - 1 = G \tag{57}$$

Specification of θ, p_h, p_l, P^A, P^B, $L_{i(h)}$, t, and y_o^A allow Eqs. (18), (20), and (53) to be evaluated as described in the section on the iteration method. However, standard iteration algorithms were found to be divergent for these equations and the following method was used.

Equations (18), (20), and (53) were first evaluated by *assuming values of* y_o^A ranging from x_i^A to 1.0, in increments of 0.1. A set of values was next calculated for the quantity G from Eq. (57), corresponding to the selected y_o^A's. The G's thus obtained were examined to determine which value in the set was the smallest in magnitude. The corresponding value of y_o^A (designated for convenience as y_o^{A*}) was then used in the next step of the computation, which consisted in reevaluating Eqs. (18), (20), and (53) for assumed values of y_o^A ranging from $(y_o^{A*} - 0.1)$ to $(y_o^{A*} + 0.1)$, in increments of 0.01. The smallest value of G was then again determined from Eq. (57). This process was repeated with increments of 0.001, 0.0001, etc., to give as many digits in y_o^A as were desired. The value of x_o^B was obtained from Eq. (56). It should be noted that in determining the smallest value of G, a check had to be applied to ensure that x_o^A was at no time smaller than zero.

Program 1-NM

The third program employed the Weller method for the case of no mixing. Details of the procedure have already been discussed. The General Electric Time-Sharing Library program NUMINT*** was employed as a subroutine in this program to evaluate the integral in Eq. (43), which expresses the required membrane area.

Program 2-NM

The fourth program was written for the Naylor and Backer method for the case of no mixing. Specification of P^A, P^B, p_h, and p_l allows the actual local separation factor α to be expressed as a function of x^A (see Equation (e) in the Appendix). The composition y_o^A is given by Eq. (54); however, this equation is divergent for the purpose of iteration, and consequently the following computational procedure was adopted:

Specification of x_i^A and θ permitted the computation of y_o^A for *assumed values of* x_o^A from the material balance equation:

$$y_o^A = \frac{1}{\theta}[x_i^A - (1 - \theta)x_o^A] \tag{53}$$

y_o^A was also calculated from Eq. (54) for the same θ and x_o^A's. The two values of y_o^A were then compared to find the pair with the smallest difference. This method was then continued as described for Program 2-PM, until the desired number of digits were obtained. In determining the smallest difference in y_o^A values, a check was necessary to ensure that $y_o^A < 1$ and that the partial pressure difference across the membrane ($p_h x_o^A - p_l y_o^A$) did not assume negative values.

Specification of $L_{i(h)}$ and l permitted the calculation of the membrane area from Eq. (55). The General Electric Time-Sharing Library program NUMINT*** was used as a subroutine in order to evaluate the integral appearing in this equation.

Program 3-NM

The last program employed the iteration method for the no-mixing case. The application of the iteration method to this case consists in dividing the stage into a large number of sections (100 is generally sufficient), with perfect mixing in each section; the depleted stream from each section is then considered as the feed stream for the following section. Consequently, the gas composition changes from section to section. Program 2-PM can then be used as described: selection of x_i^A, p_h, p_l, P^A, P^B, $L_{i(h)}$, and t, together with a permeated stream flow rate $[L_{o(l)}]_j$, permits the evaluation of $(y_o^A)_j$, $(y_o^B)_j$, $(x_o^A)_j$, $(x_o^B)_j$, and $\mathcal{A}_j$ for the jth section. The permeated stream $[L_{o(l)}]_j$ is a constant for each section, and the total permeated stream is given by $L_{o(l)} = \Sigma_{j=1}^{N} (L_{o(l)})_j$. The stage cut is given by $\theta = L_{o(l)}/L_{i(h)}$, and the average composition of the permeated stream is

$$y_o^A = \frac{\sum_{j=1}^{N} (L_{o(l)})_j (y_o^A)_j}{\sum_{j=1}^{N} (L_{o(l)})_j} \tag{58}$$

The feed rate for each section is given by

$$(L_{i(h)})_j = (L_{i(h)})_{j-1} - (L_{o(l)})_{j-1} \tag{59}$$

and the feed composition for each stage is $(x_i^A)_j = (x_o^A)_{j-1}$. Finally, the total membrane area is obtained from $\mathcal{A} = \Sigma_{j=1}^{N} \mathcal{A}_j$. The computation is terminated when a preselected stage cut is reached.

RESULTS AND DISCUSSION

Comparison of Computer Programs

The first two programs for the case of perfect mixing, 1-PM and 2-PM, yield by necessity identical results. However, in studies of two-component separation processes, Program 1-PM based on Weller's method requires only one-third to one-half the computing time necessary for Program 2-PM, which is based on the iteration method. This is a distinct advantage, particularly for lengthy parametric studies. On the other hand, Program 2-PM should prove more advantageous from the viewpoint of computing time for the study of multicomponent separation processes.

In the case where no mixing occurs on either side of the membrane, good agreement is obtained in the enrichment (y_o^A) and membrane-area ($\mathcal{A}$) values, respectively, calculated with Programs 1-NM and 3-NM. The former program is based on the Weller method, while the latter uses the iteration method. As in the case of perfect mixing, the Weller method requires shorter computing times for binary separations than the iteration method, while the reverse should be true for multicom-

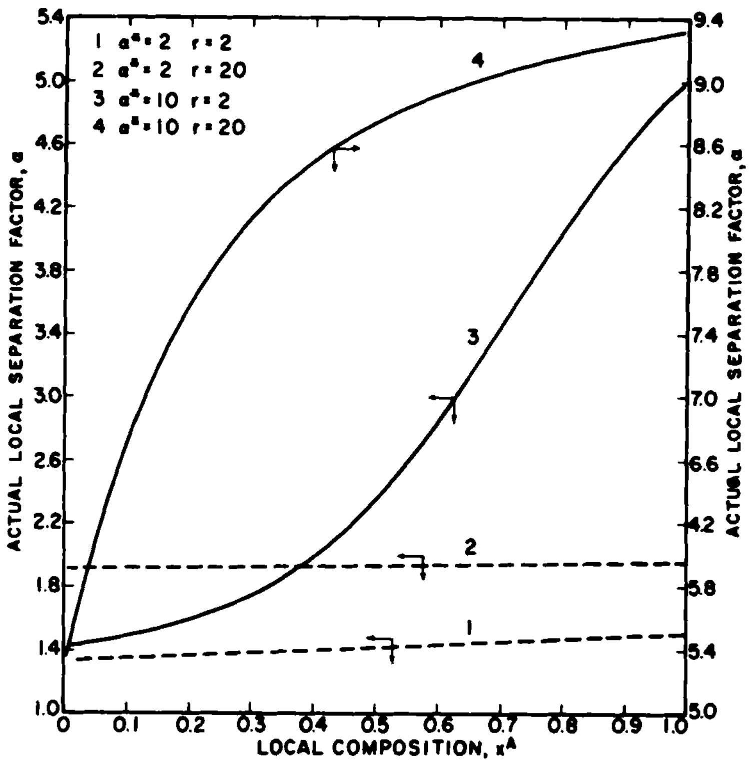

FIG. 3. Relation between the actual local separation factor α and the local composition x^A for no-mixing conditions. Effect of ideal separation factor α^* and pressure ratio r.

ponent separations. However, the iteration method offers the distinct advantage of permitting the selection of the stage cut, whereas in the Weller method the desired cut must be determined by trial and error. Consequently, when calculations are to be made for specified stage cuts, Program 3-NM may require shorter computing times than 1-NM even for binary separations.

Program 2-NM, which was written for the Naylor and Backer method, yields enrichment values that are in satisfactory agreement with those obtained by means of Programs 1-NM and 2-NM. However, membrane areas calculated by Program 2-NM appear to agree with those obtained from the latter two programs only if the actual local separation factor α does not vary by more than about 2% over the working range of compositions x^A on the high-pressure side of the membrane. As seen

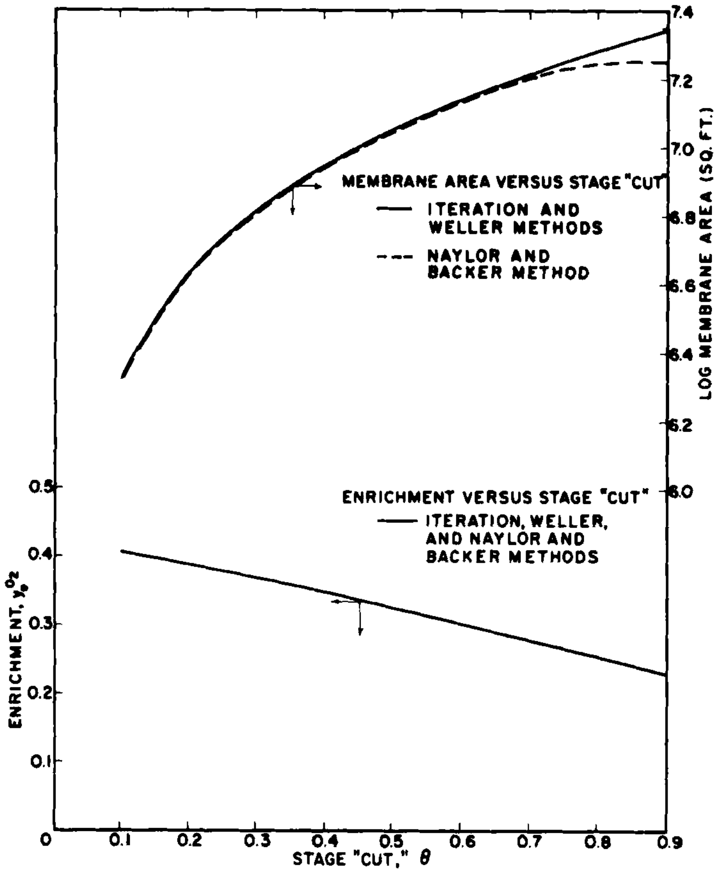

FIG. 4. Comparison between the Weller, Naylor and Backer, and iteration methods for no-mixing conditions. Dependence of membrane area and enrichment on stage cut.

from Eq. (e) in the Appendix, this would imply that the Naylor and Backer method is limited to relatively small values of the *ideal* local separation factor α^* and can be extended to higher values of α^* only when the range of x^A values is not too large. It should be noted that $\alpha \to \alpha^*$ as $\alpha^* \to 1$. Examples of the dependence of α on x^A are shown in Fig. 3 for two sets of α^* and r values. The above behavior is in agreement with the results of Hwang and Kammermeyer (*20*), who found that the Naylor and Backer method becomes equivalent with the Weller method when $\alpha = \alpha^*$. The usefulness of the Naylor and Backer method, and hence of Program 2-NM, for the estimation of membrane area requirements is therefore somewhat restricted. Finally, computing times are longer for Program 2-NM than for Program 1-NM in the case of binary separations; these programs have not been extended to multicomponent processes.

A comparison of enrichment and membrane area calculations made with the three programs for the no-mixing case, namely, 1-NM, 2-NM, and 3-NM, is presented graphically in Fig. 4. The process considered is the single-stage separation of oxygen from air by means of an ethyl cellulose membrane, as proposed by Weller and Steiner (*2*, *3*). The operating conditions used are the same as selected by these investigators and are shown in Table 1. It should be noted in Fig. 4 that the Naylor and Backer method predicts lower membrane area requirements at large stage cuts than the other two methods, for the selected conditions.

TABLE 1

Operating Conditions for Separation of Oxygen from Air by Permeation Through Ethyl Cellulose Membranes[a]

Feed rate	3984 ft^3 air/min
Feed composition	20.9% O_2 and 79.1% N_2
Membrane thickness	1×10^{-3} in. (1 mil)
Temperature	30°C
Pressures:	
On high-pressure side	8 atm
On low-pressure side	1 atm
Permeability coefficients:[b]	
For oxygen (P^{O_2})	$6.6 \times 10^{-5} \dfrac{\text{ft}^3\text{(STP) mil}}{\text{min ft}^2\text{ atm}}$
For nitrogen (P^{N_2})	$1.94 \times 10^{-5} \dfrac{\text{ft}^3\text{(STP) mil}}{\text{min ft}^2\text{ atm}}$
Ideal separation factor α^*	3.4
Flow conditions	No mixing on either side of membrane

[a] The units are those employed by Weller and Steiner (*2*, *3*).

[b] Conversion factor:

$$1 \frac{\text{ft}^3\text{(STP) mil}}{\text{min ft}^2\text{ atm}} = 1.46 \times 10^{-5} \frac{\text{cm}^3\text{(STP) cm}}{\text{sec cm}^2\text{ cm Hg}}$$

Parametric Studies

In these studies, the separation of oxygen from air in a single stage was again chosen as an example of practical interest, assuming that air was a binary gas mixture consisting of 20.9 mole % O_2 and 79.1 mole % N_2. The concentration of oxygen in the permeate stream (the oxygen enrichment) and the membrane area were calculated as a function of the fraction of the feed permeated, i.e., the stage cut. The effect of the following parameters was examined: (1) the ratio of pressures on the two sides of the membrane, when maintaining the pressure on *either* side constant and varying the pressure on the opposite side; (2) the pressure level at constant pressure ratio; and (3) the ideal separation factor.

A feed rate of 1×10^6 cm^3(STP)/sec, or about 123 tons/day, was used in all calculations. Hence, the output of the permeation process under consideration is equivalent to that of a very small cryogenic plant for air separation. Since the product is oxygen-enriched air rather than high-purity oxygen, it is interesting to note that present-day economics would probably preclude the construction of such a small cryogenic plant. The enriched air probably would be produced by evaporation of liquid oxygen and dilution of the pure oxygen gas thus obtained with the appropriate amounts of atmospheric air.

It was further assumed that the separation would be performed by means of a hypothetical membrane with a permeability coefficient for oxygen, the more rapidly permeating gas, of 5×10^{-8} cm^3(STP) cm/sec cm^2 cm Hg. The selected permeability is of the same order as found for silicone rubber (poly [dimethyl siloxane]) membranes at ambient temperature (*4*, *5*). Silicone rubber appears to exhibit the highest intrinsic permeability to oxygen of all the synthetic polymeric membranes available at present. The permeability coefficient for nitrogen, and hence the ideal separation factor, was allowed to vary. The thickness of the membrane was taken to be 2.54×10^{-3} cm (1 mil).

In all calculations, perfect mixing was assumed to take place on both sides of the hypothetical membrane. This assumption yields conservative results as compared to the case of no mixing, both in terms of larger membrane-area requirements and lower oxygen enrichments. The perfect-mixing and no-mixing cases are compared in Fig. 5 for two different values of α^* and r, when the low-pressure side is maintained at 38 cm Hg. As seen in this figure, the difference between the two cases is not very significant at low α^* values. From the viewpoint of practical applications, both the perfect-mixing and the no-mixing cases undoubtedly represent idealized situations. This has been pointed out by Breuer and Kammermeyer (*19*), who have examined the effect of concentration gradients parallel and perpendicular to the membrane for a

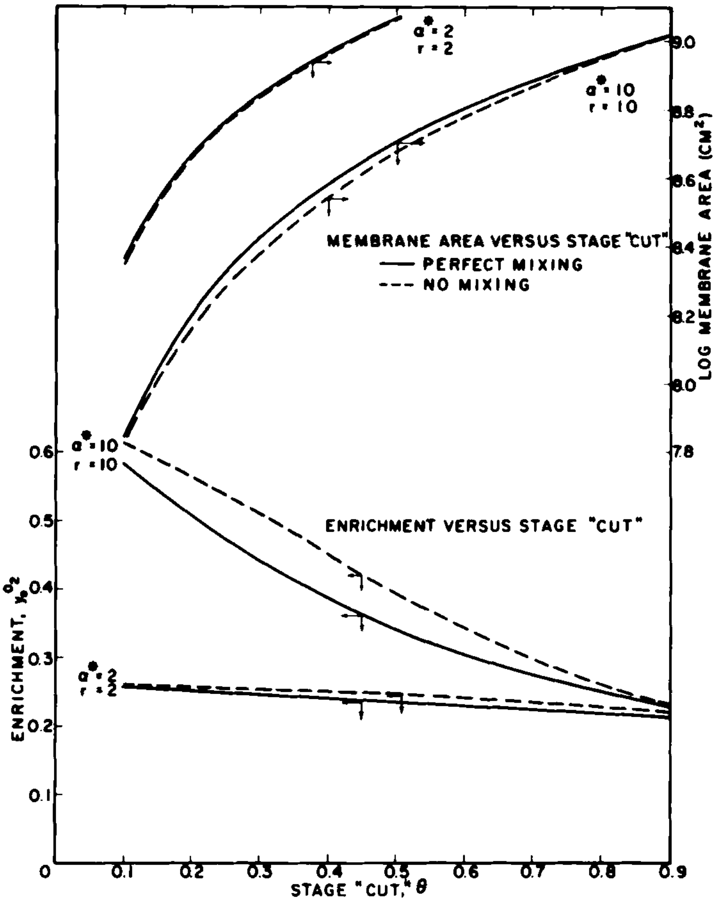

FIG. 5. Comparison between perfect-mixing and no-mixing conditions. Dependence of membrane area and enrichment on the stage cut, as a function of the ideal separation factor α^* and the pressure ratio r.

no-mixing model. Other types of stage flow-patterns, such as counterflow on opposite sides of the membrane, are also possible and have been studied by Oishi et al. (*21*).

The effect of the ideal separation factor α^* on membrane area and oxygen enrichment is shown in Table 2 for various stage cuts. The low-pressure side of the membrane was assumed to be held at 19 cm Hg and a value of 10 was selected for the pressure ratio r. The area and pressure units are consistent with the permeability coefficients, which are ex-

TABLE 2

Effect of Ideal Separation Factor on Membrane Area and Oxygen Enrichment[a]

Stage cut θ	Membrane area ($\text{cm}^2 \times 10^{-8}$)				Enrichment (Mole-fraction O_2)			
	$\alpha^* = 2$	$\alpha^* = 5$	$\alpha^* = 10$	$\alpha^* = 100$	$\alpha^* = 2$	$\alpha^* = 5$	$\alpha^* = 10$	$\alpha^* = 100$
0.1	0.492	0.893	1.31	3.24	0.319	0.486	0.612	0.898
0.2	0.988	1.85	2.87	12.5	0.310	0.458	0.565	0.795
0.3	1.49	2.89	4.74	32.0	0.301	0.427	0.511	0.642
0.4	2.00	4.01	6.94	57.7	0.291	0.394	0.452	0.512
0.5	2.51	5.21	9.43	85.9	0.280	0.359	0.394	0.416
0.6	3.04	6.50	12.2	115.0	0.269	0.324	0.342	0.348
0.7	3.57	7.86	15.0	137.0	0.256	0.291	0.297	0.299
0.8	4.11	9.27	17.9	146.0	0.242	0.259	0.261	0.261
0.9	4.67	10.7	20.6	146.0	0.227	0.232	0.232	0.232

[a] Pressure ratio $r = 10$; low pressure $p_\ell = 19$ cm Hg. Perfect mixing conditions.

TABLE 3

Effect of Pressure Ratio on Membrane Area and Oxygen Enrichment for Constant High Pressure[a]

Stage cut θ	Membrane area ($cm^2 \times 10^{-8}$)				Enrichment (mole-fraction O_2)			
	$r = 2$	$r = 5$	$r = 10$	$r = 20$	$r = 2$	$r = 5$	$r = 10$	$r = 20$
0.1	0.980	0.535	0.447	0.409	0.319	0.437	0.486	0.512
0.2	1.98	1.100	0.926	0.852	0.310	0.414	0.458	0.481
0.3	3.00	1.70	1.44	1.34	0.300	0.390	0.427	0.447
0.4	4.04	2.33	2.00	1.86	0.290	0.364	0.394	0.410
0.5	5.11	3.00	2.60	2.44	0.279	0.338	0.359	0.370
0.6	6.21	3.71	3.25	3.06	0.267	0.310	0.324	0.331
0.7	7.33	4.45	3.93	3.71	0.255	0.283	0.291	0.294
0.8	8.50	5.23	4.63	4.39	0.241	0.257	0.259	0.260
0.9	9.70	6.03	5.36	5.08	0.226	0.232	0.232	0.232

[a] Ideal separation factor $\alpha^* = 5$; high pressure $p_h = 380$ cm Hg. Perfect mixing conditions.

TABLE 4

Effect of Pressure Ratio on Membrane Area and Oxygen Enrichment for Constant Low Pressure[a]

Stage cut θ	Membrane area (cm^2 × 10^{-8})				Enrichment (mole-fraction O_2)			
	$r = 2$	$r = 5$	$r = 10$	$r = 20$	$r = 2$	$r = 5$	$r = 10$	$r = 20$
0.1	4.51	0.855	0.328	0.144	0.350	0.534	0.612	0.650
0.2	9.17	1.82	0.718	0.318	0.337	0.495	0.565	0.601
0.3	14.0	2.92	1.19	0.533	0.323	0.454	0.511	0.541
0.4	19.0	4.14	1.73	0.796	0.309	0.411	0.452	0.473
0.5	24.2	5.49	2.36	1.10	0.294	0.369	0.349	0.405
0.6	29.6	6.95	3.04	1.43	0.279	0.329	0.342	0.346
0.7	35.2	8.48	3.75	1.77	0.263	0.292	0.297	0.298
0.8	41.0	10.1	4.47	2.12	0.246	0.260	0.261	0.261
0.9	47.1	11.7	5.15	2.40	0.228	0.232	0.232	0.232

[a] Ideal separation factor $\alpha^* = 10$; low pressure $p_\ell = 76$ cm Hg. Perfect mixing conditions.

pressed herein in cm^3(STP) cm/sec cm^2 cm Hg; although widely used, these permeability units are unsatisfactory from both dimensional and practical viewpoints (*22*). As can be seen from Table 2, the membrane area and the enrichment increase with increasing α^* for specified stage cuts. The increase in membrane area is a consequence of the manner in which α^* is increased, namely, the permeability coefficient for oxygen is held constant while that for nitrogen is decreased. The membrane area could be reduced, of course, under these conditions, by reducing the feed rate. It is interesting to note that the effect of α^* on enrichment becomes relatively unimportant for stage cuts larger than about 0.6.

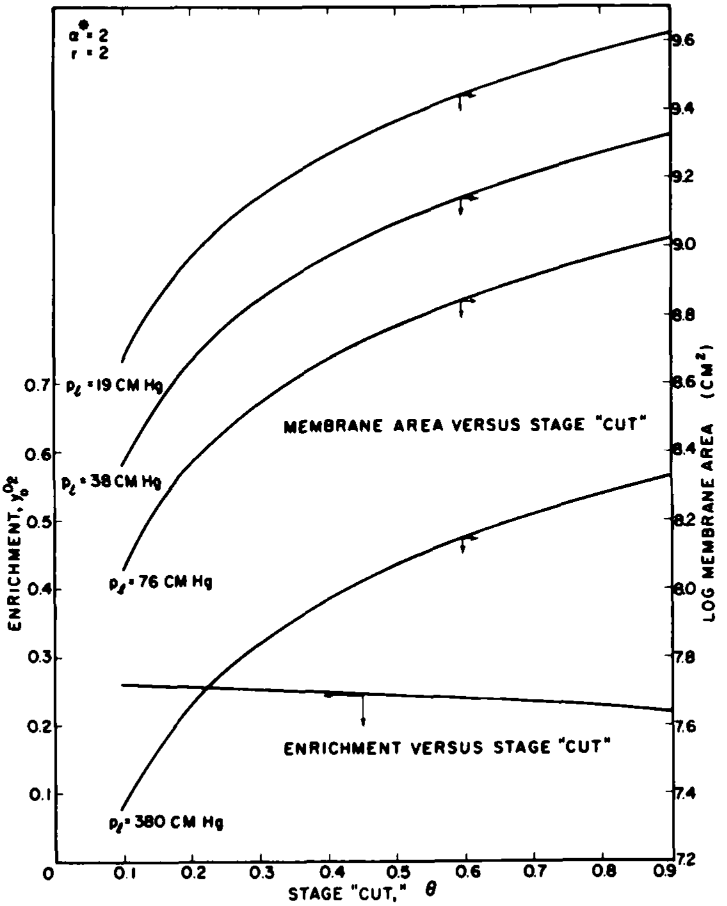

FIG. 6. Effect of pressure level on membrane area and stage cut for no-mixing conditions. The curves were obtained for $\alpha^* = 2$ and $r = 2$.

The effect of the pressure ratio r on membrane area and oxygen enrichment is shown in Tables 3 and 4. In Table 3, the high-pressure side of the membrane was assumed to be maintained at a constant pressure p_h of 380 cm Hg, while the pressure p_l on the opposite side was allowed to vary. A value of 5 was selected for the ideal separation factor. It is seen that increasing the pressure ratio in this manner, at constant θ, results in a small decrease in membrane area and a small increase in enrichment. In Table 4, p_l was taken to be constant at 76 cm Hg, and p_h was allowed to assume different values. A larger ideal separation factor of 10 was selected for this example. The membrane area and enrichment are seen to exhibit the same trends as in Table 3, but both the decrease in the former and the increase in the latter are more pronounced.

The effect of pressure level on membrane area and oxygen enrichment is shown graphically in Fig. 6 for an ideal separation factor of 2 and a pressure ratio of 2. The membrane area is inversely proportional to the pressure level, at constant pressure ratio, as evident also from Eq. (18). On the other hand, the enrichment is independent of pressure level and, for a given feed composition, is a function of only the pressure ratio, the ideal separation factor, and the stage cut. This can be seen also by comparing, for instance, the enrichment values for $\alpha^* = 5$ and $r = 10$ in Tables 2 and 3, or the values for $\alpha^* = 10$ and $r = 10$ in Tables 2 and 4.

Similar relations are obtained for the case where no mixing occurs on either side of the membrane. Membrane area requirements for larger or smaller feed rates can be obtained directly from the above results, since the membrane area is directly proportional to feed rate.

SUMMARY AND CONCLUSIONS

This investigation has shown that the Weller and iteration methods can be programmed satisfactorily for parametric studies of binary separation processes, both for perfect mixing and for no-mixing cross-flow conditions. The Weller method generally requires shorter computing times, except when data are desired for specified stage cuts in the no-mixing case. The iteration method should be preferable for multicomponent separations from the viewpoint of computing-time requirements. The Naylor and Backer method is of more limited usefulness, being restricted to small values of the ideal separation factor.

The question whether the stage flow patterns studied here are realistic or not can be answered only in relation to a specific permeator design.

Several types of permeators for large-scale applications (spiral, flat-plate, etc.) have been described in the technical and patent literature, but detailed mass-transfer studies in such devices either have not been made or have not been disclosed. The theoretical work of Oishi et al. (*21*) indicates that counterflow on the two sides of a membrane is one of the most efficient flow patterns in terms of achievable enrichment, while perfect mixing is one of the least efficient. Other flow patterns, such as cross-flow with no mixing on either side of the membrane, yield enrichments that lie in between the values obtained in these two limiting cases. As has been mentioned previously, the perfect-mixing case is useful for preliminary evaluations because it provides conservative estimates of membrane area requirements and enrichments.

The partial separation of a 20.9 mole % O_2–79.1 mole % N_2 mixture, simulating the enrichment of an air stream in oxygen, has been studied as an example of a single-stage gas-permeation process. The separation was assumed to be performed by means of a hypothetical membrane exhibiting a permeability to oxygen similar to that reported for silicone rubber at ambient temperature. Perfect mixing was assumed to occur on both sides of the membrane. The dependence of the membrane area and oxygen enrichment on the ideal separation factor, ratio of pressures on the two sides of the membrane, pressure level, and stage cut was determined for selected values of these parameters. The results of these calculations are presented in Tables 2, 3, and 4, and in Figs. 3, 4, and 5. Similar relations and trends are found also for the no-mixing case, although the shapes of the enrichment versus stage cut curves are somewhat different. The large membrane areas calculated for the assumed conditions confirm that the capital investment costs of an air-separation process based on selective permeation will be very high, even if it is assumed that permeator costs can be reduced to as little as \$1.00/ft^2 of membrane (installed). In other words, the permeation process will not be competitive with the conventional cryogenic method of air separation. Large membrane-area requirements are characteristic of most of the gas-permeation processes of industrial interest that have been investigated, and are due to the relatively low gas permeabilities of the polymeric membranes available at present.

The membrane-area requirements could be reduced by one or more of the following methods: (a) synthesis of more permeable membrane materials, (b) preparation of very thin membranes, and (c) optimization of operating conditions. The synthesis of membranes that are more permeable to specific gases will have to rely to some extent on trial and error, because the effect of membrane composition and morphology on permeation mechanism is not well understood. A considerable amount of synthesis work is presently in progress in many industrial laboratories; unfortunately for the problem under consideration, most of this work appears to be directed towards the development of *less* permeable membranes for packaging applications. Nevertheless, progress is being made in this area, as witnessed by the recent development of highly effective perfluoro membranes for helium recovery (*8*). Various methods of preparing very thin membranes are also being developed. However, in the particular case of air separation, it has been reported that even 2.54×10^{-4} cm (0.1 mil)-thick silicone rubber membranes are not sufficiently permeable to oxygen for an economically competitive permeation process (*6*). Finally, the choice of optimum operating conditions will depend on the permeation behavior of specific gas–membrane systems. It would be interesting to examine, for example, whether or not it is economically advantageous to increase the pressure level on *both* sides of the membrane; operating costs could then be reduced by suitable energy-recovery devices. In previous studies, it was generally assumed that the low-pressure side of the membrane would be maintained at atmospheric or below-atmospheric levels.

Although ideal separation factors as large as 20 have been used in these calculations for illustrative purposes, it should be noted that in the case of air separation these values are entirely hypothetical. For a large variety of real membranes, the ideal separation factor for oxygen–nitrogen mixtures was found to vary only between about 2 and 5, although the absolute permeability of the membranes to oxygen and nitrogen varied by six orders of magnitude (*6*). As a result, the separation of high-purity oxygen from air by selective permeation probably would require five or six permeation stages in series; the high interstage recompression costs would render such a process uneconomical, even if the absolute permeability of the membranes could be greatly increased. For other permeation processes of industrial interest, however, the ideal separation factors could be as large as, or larger than, the maximum value of 20 used in this study.

Finally, it should be noted that all calculations reported herein are based also on the implicit assumption that the permeability coefficients are independent of pressure. Recent studies have shown that this assumption is satisfactory for oxygen, nitrogen, and other gases with critical temperatures that are low compared to the expected operating temperature of a practical permeation process. On the other hand, the permeability coefficients for gases with relatively high critical temperatures appear to be strongly dependent on pressure (*23–25*); this behavior must be taken into account when studying the separation of mixtures of such gases by selective permeation.

APPENDIX

The Separation Factor

It has been mentioned that the *local* permeation rates of the components A and B of a binary mixture across an element of membrane area $d\mathcal{A}$ can be expressed, at steady-state, by Eqs. (21) and (22). The ratio of these expressions is

$$\frac{y^A}{1-y^A} = \left(\frac{p^A}{p^B}\right)\frac{x^A-(1/r)y^A}{(1-x^A)-(1/r)(1-y^A)} \tag{a}$$

where r ($= p_h/p_l$) is the ratio of total pressures on the two sides of the membrane ($p_h > p_l$).

The *actual* local or point separation factor α is defined as usual

$$\alpha = \frac{y^A/(1-y^A)}{x^A/(1-x^A)} \tag{b}$$

Equations (a) and (b) yield the expression

$$\alpha = \left(\frac{P^A}{P^B}\right)\left(\frac{(1-x^A)/(1-y^A)}{[(1-x^A)/(1-y^A)] + (1/r)[(P^A/P^B)-1]}\right) \tag{c}$$

The ratio

$$\alpha^* = \frac{p^A}{p^B} \tag{d}$$

is known as the *ideal* local or point separation factor, and depends only on the nature of the gas–membrane system under consideration and the temperature. If Eq. (b) is used to eliminate y from Eq. (c), the following relation is obtained for the actual local separation factor:

$$\alpha = \frac{(\alpha^*+1)}{2} - \frac{(1/r)(\alpha^*-1)}{2} - \frac{1}{2x^A} \pm \left\{\left(\frac{\alpha^*-1}{2}\right)^2 + \frac{(\alpha^*-1)-(1/r)[(\alpha^*)^2-1]}{2x^A} + \left[\frac{(1/r)(\alpha^*-1)+1}{2x^A}\right]^2\right\}^{1/2} \tag{e}$$

Only the positive root is used. Hence, α depends on α^*, the pressure ratio r, and the local composition x^A of the more permeable component on the high-pressure side of the membrane. It is seen that

$$\alpha \longrightarrow \alpha^* \quad \text{when} \quad r \longrightarrow \infty$$

i.e., the actual separation factor reduces to the ideal separation factor when $p_l \longrightarrow 0$.

The actual and ideal enrichment factors

$$\epsilon \equiv \alpha - 1 = \frac{y^A - x^A}{x^A(1 - y^A)} \tag{f}$$

and

$$\epsilon^* \equiv \alpha^* - 1 \tag{g}$$

respectively are used sometimes instead of the corresponding separation factors.

In the calculation of separation cascades, it is convenient to use the concept of *stage* separation factor. This factor is also defined by Eq. (b), with y^A and x^A being the compositions of the more permeable component in the permeated and nonpermeated streams leaving the stage, i.e., $y^A_{o(l)}$ and $x^A_{(o)h}$, respectively. In the perfect-mixing case, the actual local or point separation factor has a constant value across any stage and is identical with the stage separation factor. In the no-mixing case, the actual local separation factor varies with composition as indicated by relation (e).

It should be noted that for *porous* membranes, the use of Eqs. (44) and (45) in conjunction with Eq. (b) also leads to expression (e) for the actual local separation factor, as found for nonporous membranes. However, the ideal local separation factor assumes in the former case the well-known form

$$\alpha^* = \left(\frac{M^B}{M^A}\right)^{1/2} \quad \text{for} \quad r \longrightarrow \infty \tag{h}$$

where A is the lighter component.

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