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A MEMBRANE GAS SEPARATION EXPERIMENT FOR THE UNDERGRADUATE LABORATORY

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Synthetic membranes have been the focus of much attention recently because of their simple and economical operation for separating gases. The Permea Corporation offers a Prism® separator package as a laboratory-scale system for demonstrating membrane gas separation. The apparatus consists of four columns, with each column being two inches in diameter and four feet long and filled with bundles of hollow fibers. The system can be conveniently used to separate oxygen from the air. We purchased one of the units, have used it in our required senior laboratory course for the past three years, and have found it straightforward to operate.

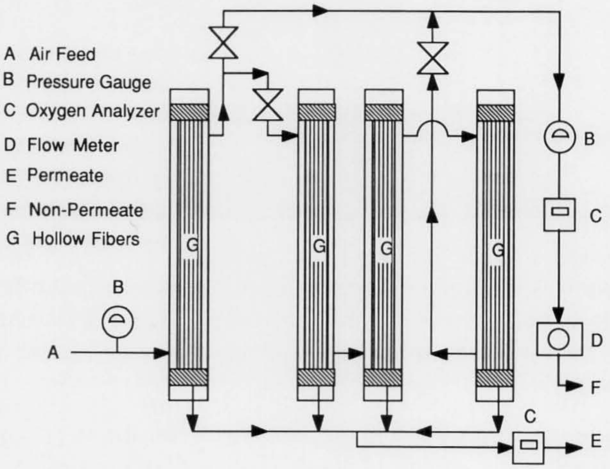
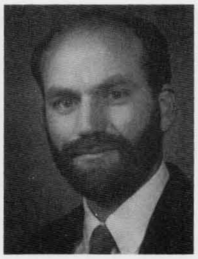


FIGURE 1. *Flow diagram for laboratory scale Prism® separator system.*

For the first two years the suggested objective for the students was to determine the effects of pressure and feed-flow rate on the degree of separation. The data analysis required to meet this objective involved only overall mass balances. We felt that the experience was not satisfactory for senior-level chemical engineering students, so we modified the apparatus and changed the objectives of the experiment in order to make the apparatus more suitable for our laboratory. The plumbing was modified so that measurements could be taken either on a single column or on the original four-column arrangement. An analysis was carried out and software was written for the single-column data in order to determine the transport properties needed to predict membrane performance. A software package was also developed to use these parameters as determined from the single-column data in order to predict the air separation to be achieved with the four-column arrangement and to compare with the observed data.



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This paper describes the new objectives and procedures that were used to increase the technical content of the experiment and to teach the students about the fundamental mass-transfer characteristics of membranes.

EXPERIMENTAL DESIGN

The experimental apparatus consists of four Prism® separator columns arranged as shown in Figure 1. Each column contains thousands of nonporous, semipermeable membranes in the form of

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hollow fibers. The oxygen permeates through the fiber walls and is collected in a manifold at the bottom of the separator. The less-permeable nitrogen passes through the column and exits from the top of the separator.

A column consists of a shell with a hollow-fiber membrane tube-bundle potted at each end, similar to a shell-and-tube heat exchanger.[1] A filtered, compressed-air stream is fed to the bottom of the first column. The high-pressure air stream, fed to the bottom of the first column, flows through on the shell side of the membrane tube-bundle. The pressure is measured at both the feed and outlet of the high pressure, non-permeate stream. The hollow-fiber tube bundles are capped at the top so that the permeate, or oxygen-rich, streams leave from the hollow-fiber membranes at the bottom of each column. The permeate streams are arranged in parallel and exit through a common manifold. The non-permeate streams are connected in series. Thus, the first and third separators operate in counter-current flow conditions, and the second and fourth separators operate in a cocurrent flow pattern. Two oxygen analyzers measure the percent of oxygen in the exit non-permeate and the permeate streams. The exit stream of the non-permeate side is connected to a volumetric flow meter. The flow rate of the feed and permeate streams can be calculated by mass balances.

The original apparatus allowed for only a four-column separation. The system was modified so that measurements could also be made on a single column. In single-column operation, the conditions are counter-current flow, and such a modification enables the student to determine the important membrane transport properties from measurements taken on a single column.

The objectives of the experiment are:

1. *To determine the separation factor as a function of pressure and non-permeate feed flow rate for mass transfer in a single separator. The separation factor is defined as*

$$\alpha = \frac{\left([O_2]/[N_2]\right)\ O_2 \text{ enriched stream}}{\left([O_2]/[N_2]\right)\ N_2 \text{ enriched stream}} \tag{1}$$

   and to compare this with the ideal separation factor defined as the ratio of the permeabilities of the more-permeable species ($A = O_2$) to the less-permeable species ($B = N_2$)

$$\alpha^* = \frac{Q_A}{Q_B} \tag{2}$$

2. *To predict the exit oxygen concentration of the non-permeate stream for the four-column setup based on the analysis of the first separator. This should be repeated for several pressures and flow rates and compared with actual values from experiments.*
3. *To compare the degree of separation between cocurrent and counter-current flow conditions.*

THEORY

The membrane separators are modeled with the assumption that air passes through the column with no axial diffusion or mixing. It is also assumed that the amount of gas permeating is small enough and that the feed gas rate is low enough so there is no axial pressure drop on either side of the membrane. This is a good assumption for the apparatus described here with the high-pressure feed passing on the outside of the hollow-fiber tubes.[2] The other critical assumptions are that the membrane is homogeneous, that the gas permeabilities are constant, and that there is no gas phase mass transfer resistance.

The governing equations presented here are well-known.[3,4] The equations are developed here for cocurrent flow conditions (see Figure 2). The results for a counter-current flow pattern are presented after this derivation.

For cocurrent flow conditions, the flux of O_2 from the high-pressure side to the low-pressure side in a volume element is described, using Fick's Law and assuming ideal gas behavior, by

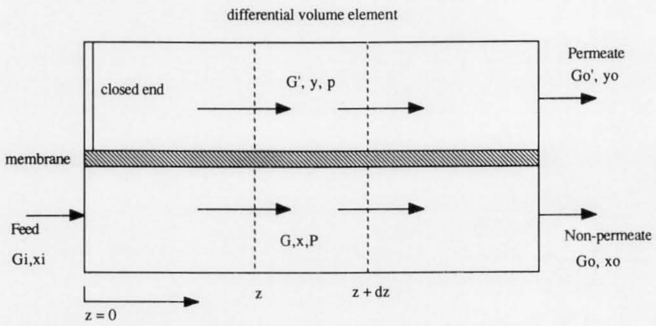

FIGURE 2. *Diagram of a separator with cocurrent flow conditions.*

$$-\,d(Gx)=\left(\frac{Q_A}{\delta}\right)(Px-py)\,dA \tag{3}$$

The flux of N_2 is described by

$$-\,d\big[G(1-x)\big]=\left(\frac{Q_B}{\delta}\right)\big[P(1-x)-p(1-y)\big]\,dA \tag{4}$$

where the differential area is

$$dA=a\,dV=\frac{a\pi d^2}{4}\,dz \tag{5}$$

In these equations, Q_A and Q_B are the permeabilities of oxygen and nitrogen, respectively; δ is the membrane thickness; a is the interfacial membrane area per unit volume of separator; and d is the inner diameter of the column.

The equations are difficult to solve as they stand. Also, the values for Q_A, Q_B, A, and δ are unknown for the apparatus. These problems are avoided by combining the unknown parameters and making use of a more convenient form developed by Walawender and Stern.[3] These authors use the overall material and species balances for O_2 (Eqs. 6 and 7) together with the flux equations (Eqs. 3 and 4) to formulate the differential equations describing the concentration profiles for O_2 in the non-permeate and permeate streams.

$$G_i=G+G' \tag{6}$$

$$G_i\,x_i=Gx+G'y \tag{7}$$

The combined form of Eqs. (3) through (7) is

$$G_i\frac{dx}{dA}=\left(\frac{x-y}{y-x_i}\right)\left[(1-x)\left(\frac{Q_A}{\delta}\right)(Px-py)-x\left(\frac{Q_B}{\delta}\right)\big[p(1-x)-p(1-y)\big]\right] \tag{8}$$

$$G_i\frac{dy}{dA}=\left(\frac{x-y}{x-x_i}\right)\left[(1-y)\left(\frac{Q_A}{\delta}\right)(Px-py)-y\left(\frac{Q_B}{\delta}\right)\big[p(1-x)-p(1-y)\big]\right] \tag{9}$$

The equations are further simplified by substituting the ideal separation factor, α^*, the dimensionless differential height, z^*, and r, the ratio of the high to low pressures, to give

$$r=\frac{P}{p} \tag{10}$$

$$K\frac{dx}{dz^*}=\left(\frac{x-y}{y-x_i}\right)\Big[(1-x)\alpha^*(rx-y)-x\big[r(1-x)-(1-y)\big]\Big] \tag{11}$$

$$K\frac{dy}{dz^*}=\left(\frac{x-y}{x-x_i}\right)\Big[(1-y)\alpha^*(rx-y)-y\big[r(1-x)-(1-y)\big]\Big] \tag{12}$$

where

$$K=\frac{G_i}{\left(\frac{Q_B}{\delta}\right)ph\,\frac{a\pi d^2}{4}}=\frac{4\,G_i\delta}{Q_B\,ph\,a\pi d^2} \tag{13}$$

K and α^* become the key transport parameters that describe the separation process.

The value of y_i at the closed end, which is needed to integrate Eqs. (11) and (12), can be evaluated by noting that $G'=0$ at $z=0$.[3,5] The ratio of Eqs. (3) and (4), with the appropriate substitutions of α^* and r, becomes

$$\frac{d(G'y)}{d\big[G'(1-y)\big]}=\frac{a^*(rx-y)}{r(1-x)-(1-y)} \tag{14}$$

The left-hand side of Eq. (14) can be rearranged to the following form:

$$\frac{d(G'y)}{d\big[G'(1-y)\big]}=\frac{y}{1-y}+\frac{G'dy}{(1-y)\,d\big[G'(1-y)\big]} \tag{15}$$

At z = 0, the last term in Eq. (15) vanishes, and the result is substituted into Eq. (14), yielding a quadratic equation for y_i

$$\frac{y_i}{1-y_i}=\frac{a^*(rx_i-y_i)}{r(1-x_i)-(1-y_i)} \tag{16}$$

Eq. (16) can be solved for y_i

$$y_i=\frac{(\alpha^*-1)(rx_i+1)+r-\sqrt{\big[(\alpha^*-1)(rx_i+1)+r\big]^2-4\alpha^* rx_i(\alpha^*-1)}}{(2\alpha^*-1)} \tag{17}$$

Eq. (12) is indeterminate as z approaches 0, and special consideration is required to evaluate the derivative at z = 0, which is needed to start the numerical integrations. L'Hopital's rule[3,4] is used to obtain this value

$$\left.\left(\frac{dy}{dz^*}\right)\right|_{z^*=0}=\frac{(x_i-y_i)r\big[\alpha^*-y_i(\alpha^*-1)\big]}{K-\dfrac{\Big[(x_i-y_i)\big[(\alpha^*-1)(2y_i-rx_i-1)-r\big]\Big]}{\left.\left(\dfrac{dx}{dz^*}\right)\right|_{z^*=0}}} \tag{18}$$

Integration of Eqs. (11) and (12) describes the separation that will be achieved for cocurrent operation.

The flow pattern for counter-current conditions is shown in Figure 3. The final form of the governing equations is

$$K'\frac{dx}{dz^*}=-\left(\frac{x-y}{y-x_o}\right)\Big[(1-x)\alpha^*(rx-y)-x\big[r(1-x)-(1-y)\big]\Big] \tag{19}$$

$$K'\frac{dy}{dz^*}=-\left(\frac{x-y}{x-x_o}\right)\Big[(1-y)\alpha^*(rx-y)-y\big[r(1-x)-(1-y)\big]\Big] \tag{20}$$

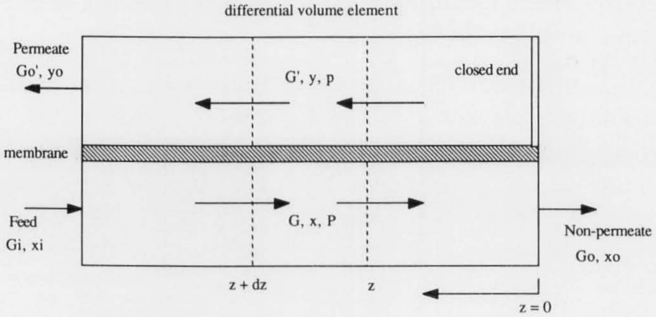

FIGURE 3. *Diagram of a separator with counter-current flow conditions.*

$$K' = \frac{G_o}{\left(\frac{Q_B}{\delta}\right) ph \frac{a\pi d^2}{4}} = \frac{4 G_o \delta}{Q_B \, p h a \pi d^2} \tag{21}$$

In this case, the value of y_i at the closed end is

$$y_i = \frac{\left(\alpha^* - 1\right)\left(r x_o + 1\right) + r - \sqrt{\left[\left(\alpha^* - 1\right)\left(r x_o + 1\right) + r\right]^2 - 4\alpha^* r x_o \left(\alpha^* - 1\right)}}{\left(2\alpha^* - 1\right)} \tag{22}$$

Eq. (20) at z = 0 becomes

$$\left.\left(\frac{dy}{dz^*}\right)\right|_{z^*=0} = \frac{(x_o - y_i) r \left[\alpha^* - y_i\left(\alpha^* - 1\right)\right]}{K - \frac{\left\{(x_o - y_i)\left[\left(\alpha^* - 1\right)\left(2y_i - r x_o - 1\right) - r\right]\right\}}{\left.\left(\frac{dx}{dz^*}\right)\right|_{z^*=0}}} \tag{23}$$

The system of non-linear initial-value differential equations is solved simultaneously by using a fourth-order Runge-Kutta numerical scheme. The required initial values are determined from experiments.

METHOD OF SOLUTION

Initially, the student is required to evaluate α^* for the O_2/N_2 membrane system and K′ as a function of the non-permeate exit stream flow rate, using data from a single column operating under counter-current flow conditions. The evaluation of α^* and K′ is accomplished by making several measurements of the non-permeate and permeate exit compositions for a range of non-permeate flow rates and pressures. The governing equations (Eqs. 19 and 20) are integrated with the known inlet and exit conditions. The only unknowns are α^* and K′. The solution requires "shooting" for the known end conditions with guesses for α^* and K′ until the experimental end conditions are met and the solution converges on the desired values for α^* and K′. This is very similar to solving a two-point boundary-value problem. A systematic procedure, based on a modified Newton method, was developed to iterate on subsequent trials for α^* and K′ until acceptable convergence criteria were satisfied. Generally, this method requires less than ten iterations to achieve convergence. The students can easily arrive at a good initial guess for α^* based on their experimental data. A reasonable estimate for K′ is more problematic. It is possible to estimate K'/G_o from data in the literature. However, since this would require a considerable amount of student time, we give the students an approximate value to start the calculation ($K'/G_o \cong 4000$ s/gmol).

The information for α^* and K′ is used to make predictions for separations in the four-column arrangement and to model the separation for comparison between cocurrent and counter-current flow patterns. Three programs are provided for the students to use. The first program requires information from experiments on the first column and solves for α^* and K′. The other two programs solve the O_2 concentration profiles for either cocurrent or counter-current flow conditions based on the initial conditions specified by the user. The required input values for all the programs are the pressure, the mole fraction of O_2, and the flow rate for the inlet high-pressure stream. The program for counter-current flow calculates K′ based on iterated computed results and mass balances. Note that for counter-current flow conditions, K′ is a function of G_o, and that K for cocurrent flow conditions is a function of G_i. This does not create a problem for our design because the columns are arranged so that each counter-current column is followed by a cocurrent column. In this case, K = K′ from the previous column.

These programs, along with mass balances, are used to make predictions for the separation that occurs in the four-column arrangement. The programs are run on an IBM PC which is located in the laboratory. Thus, the students can analyze their data while the apparatus is running, and the analysis can be used to set operating conditions. Listings of the programs developed here in True BASIC™ are available from the authors.

SAMPLE CALCULATIONS

The data for the calculations presented here are from actual student experiments. Sample data from operating the single-column arrangement are listed in Table 1. Exit O_2 mole fractions and non-permeate flow rates are reported for three feed pressures. A plot of the experimental separation factor against the feed flow rate in Figure 4 shows how pressure has a large effect on the degree of separation independent of the flow rate.

Next, the differential equations (Eqs. 19 and 20) are solved for α^* and K′, using the results from Table 1. The calculated results for α^* and K′ are also presented in Table 1. It may be seen that α^* is a constant independent of flow rate and pressure as predicted by theory, and that K′ is independent of the non-permeate pressure, P; thus the results for K′ vs G_o for the three pressures are plotted together in Figure 5. It may be seen in Figure 5 that, as expected, K′ is a linear function of flow rate. The results for K′ as a function of G_o are correlated by an equation of the form

$$K' = mG_o \tag{24}$$

where m is the proportionality constant from Eq. (21)

$$m = \frac{4\delta}{Q_B \, ph \, a\pi d^2} \tag{25}$$

For this data, a least squares fit of the results yields m = 3974 13 s/gmol. The average value for α^* is 5.90 0.11. It is immediately evident that α^* is a poor approximation for the actual separation factor, α, when this is compared with the results in Figure 4.

This information can also be used to compare cocurrent with counter-current separation in membranes operating under plug-flow conditions. Non-permeate O_2 mole fractions for these two cases are plotted against the dimensionless column length in Figure 6. The profiles are for P = 653 kPa; p = 101 kPa; G_i = 0.0117 gmol/s; and x_i = 0.21.

Next, predictions are compared with experiments for separation in the four-column arrangement. The prediction requires several mass-balance calculations and an understanding of the operating parameters. A sample calculation is given for the prediction of α for four columns with $x_{1,i}$ = 0.21; $G_{1,i}$ = 0.0355 gmol/s; P - p = 552 kPa; and T = 25 C. The numbered subscript refers to the separator column.

The first column is in counter-current flow. The differential equations for this condition are solved numerically with the initial conditions for the problem. The results give $x_{1,o}$ = 0.189 and $y_{1,o}$ = 0.502. The equations for the mass balance are

$$0.0355 = G_{1,o} + G'_{1,o}$$

$$(0.21)(0.0355) = 0.189\,G_{1,o} + 0.502\,G'_{1,o}$$

These equations are solved simultaneously for $G_{1,o} = G_{2,i}$ = 0.0331 and $G'_{1,o}$ = 0.00236 gmol/s. This value multiplied by m gives $K'_1 = K_2$ = 131.6.

The next column is cocurrent flow and the initial conditions are the results from the material balance around column 1. The numerical results are $x_{2,o}$ = 0.170 and $y_{2,o}$ = 0.460. A mass balance performed around column 2 for $G_{2,o}$ gives

$$0.0331 = G_{2,o} + G'_{2,o}$$

$$(0.189)(0.0331) = 0.170\,G_{2,o} + 0.460\,G'_{2,o}$$

The solution yields $G_{2,o} = G_{3,i}$ = 0.0309, and

Table 1
Data From a Single Column with Counter-Current Flow

P(kPa)	G_o x 10²(gmol/s)	x_o	y_o	α^*	K′
377	0.73	0.18	0.43	5.87	31.01
377	0.74	0.18	0.43	5.87	31.01
377	1.03	0.19	0.44	6.00	49.34
377	1.32	0.19	0.44	6.00	49.34
377	2.54	0.20	0.44	5.74	98.41
515	0.62	0.15	0.45	5.93	26.10
515	0.73	0.16	0.46	6.01	33.14
515	0.95	0.17	0.47	6.16	43.73
515	1.51	0.18	0.47	5.84	57.96
515	2.25	0.19	0.48	6.00	91.84
653	0.74	0.14	0.46	5.77	31.40
653	0.95	0.15	0.47	5.82	38.64
653	1.32	0.16	0.48	5.92	48.89
653	2.18	0.18	0.49	5.75	85.30
653	3.44	0.19	0.50	5.82	134.70

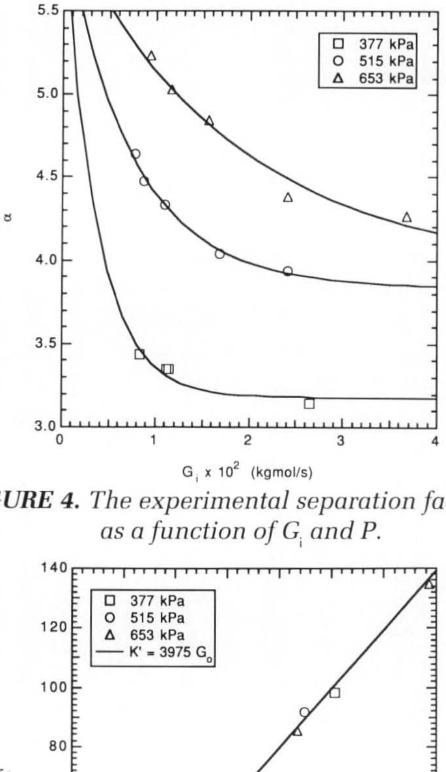

FIGURE 4. *The experimental separation factor, α, as a function of G_i and P.*

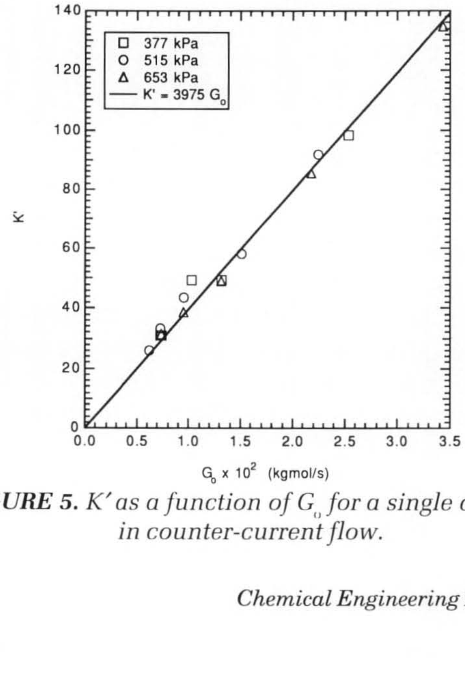

FIGURE 5. *K′ as a function of G_o for a single column in counter-current flow.*

$G'_{2,o}$ =0.00221 gmol/s.

The above procedure is repeated for the next two columns. The results are $x_{3,o} = 0.151$; $y_{3,o} = 0.429$; $G_{3,o} = 0.0287$; $G'_{2,o} = 0.00213$ kgmol/s; $x_{4,o} = 0.133$; $y_{4,o} = 0.383$; $G_{4,o} = 0.0267$; $G'_{4,o} = 0.00201$ gmol/s.

The calculation of the separation factor is not as straightforward as that for the single column. The average mole fraction of O_2 in the outlet permeate stream, y_o, is found by weighting the value of y_o from each column with the permeate flow rate

$$y_o = \frac{\sum\limits_{n=1}^{4} y_{no} G'_{no}}{\sum\limits_{n=1}^{4} G'_{no}} \tag{26}$$

This calculation gives $y_o = 0.446$. The predicted separation factor is $\alpha_p = 5.24$, which compares very well with the experimental value $\alpha_e = 5.26$. Experimental data are listed in Table 2 for several trials using four columns. The separation factors are compared with predictions from the model for several pressures and flow rates in Figure 7.

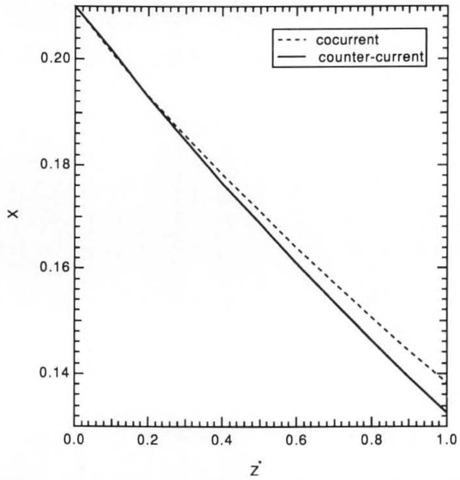

FIGURE 6. *Comparison of mole fraction profiles for co- and counter-current flow.*

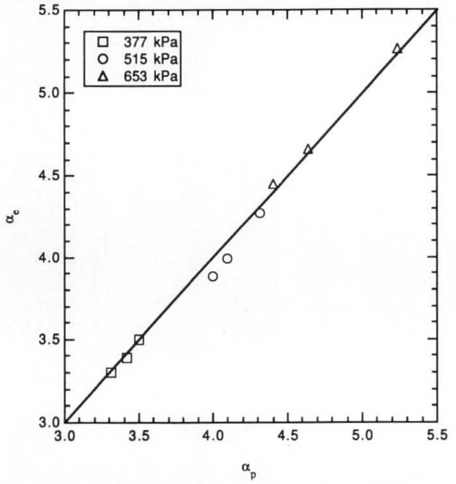

FIGURE 7. *Comparison of experimental results with predictions for separation in four columns.*

CONCLUSIONS

This membrane experiment provides the students with experience in fundamental engineering skills such as mass balances, modeling, and using the computer as a research tool. They are also exposed to a new separation method that employs membranes. Without the analysis presented here, the students are only able to carry out performance tests of the apparatus. A simple modification of the apparatus and implementation of the numerical procedure developed here permits the students to determine the appropriate transport properties of the membrane separator. Knowledge of these properties allows integration of the design equations to predict separator performance.

Our experience has been that it is too much to expect undergraduates to derive, on their own, the numerical techniques presented here. However, we find that when they are given a handout on the equation derivations, together with an explanation of the numerical procedure, they are able to define meaningful experiments in order to determine the important transport properties and are also able to predict separation performance.

Some interesting questions for the students to consider are: Why are the experimental separation factors less than the ideal separation factors? Why is the separation factor an increasing function of nonpermeate pressure and a decreasing function of gas flow rate? How can the individual units be arranged to maximize the separation?

Continued on page 21.

TABLE 2
Data From Four-Column Experiments

P(kPa)	$G_i \times 10^2$ (gmol/s)	x_o	y_o	α_e	α_p
377	2.36	0.16	0.40	3.50	3.50
377	2.77	0.17	0.41	3.39	3.42
377	3.76	0.18	0.42	3.30	3.31
515	3.30	0.15	0.43	4.27	4.31
515	4.95	0.17	0.45	3.99	4.10
515	5.82	0.18	0.46	3.88	4.00
653	3.55	0.13	0.44	5.26	5.24
653	4.66	0.15	0.44	4.45	4.40
653	6.30	0.16	0.47	4.66	4.64

GAS SEPARATION EXPERIMENT

Continued from page 15.

An evaluation survey was conducted of all the students participating in this experiment during the fall quarter of 1989. They were asked to evaluate different aspects of the modified membrane experiment, such as clarity of the handout on equation derivation, appropriateness of objectives, and ability to analyze data using the computer programs that were provided. The responses indicated that they liked the experiment, and there was a general feeling of satisfaction with their laboratory experience. As instructors, we were pleased with the outcome of our efforts to enhance the technical aspects of this experiment.

ACKNOWLEDGEMENT

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NOMENCLATURE

A = unit membrane interfacial area (m^2)
a = interfacial membrane area per unit volume of separator (m^{-1})
d = inner diameter of separator column (m)
G = molar flow rate of gas in the non-permeate stream (gmol/s)
G′ = permeate stream molar flow rate (gmol/s)
h = separator column height (m)
K = dimensionless transport parameter defined in Eq. (12)
K′ = dimensionless transport parameter defined in Eq. (20)
m = K′ correlation coefficient
P = absolute pressure in the non-permeate stream (kPa)
p = absolute pressure in the permeate stream (kPa)
Q = permeabilities (kgmol/m·kPa·s)
T = temperature (C)
V = unit volume of separator column (m^3)
x = mole fraction of O_2 in the non-permeate stream
y = mole fraction of O_2 in the permeate stream
z = distance along length of separator column (m)
z^* = z/h, dimensionless column length

Greek Symbols

α = separation factor
α^* = ideal separation factor, Q_A/Q_B
δ = membrane thickness (m)

Subscripts

A = oxygen
B = nitrogen
i = inlet
n = column number
o = exit

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