The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed 14 double-spaced pages and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

GAS PERMEATION COMPUTATIONS WITH MATHEMATICA

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Gas separations using membranes have received increased attention by the scientific and industrial community. This technique is now at a mature stage and can compete with more common techniques used in the petrochemical industry such as cryogenic separation, gas absorption, and pressure swing adsorption. The nonporous membranes can be organic or inorganic. They are classified according to their thermal and chemical stability as well as their selectivity to different gases. The mechanism of separation is based on the differences in the dissolution and diffusion of gases in the nonporous membrane. The separation of hydrogen from other gases such as carbon dioxide and carbon monoxide in syngas plants is a very important industrial application of this technique. Acid gas (CO_2 and H_2S) elimination from natural gas is another application of membrane separations. Very often one is confronted with the separation of multicomponent mixtures. Thus, we consider a hypothetical ternary mixture, in the first part of the paper, to show how one can obtain the permeate and reject compositions as well as the membrane area.

SEPARATION OF A TERNARY MIXTURE

A ternary feed mixture has the following composition and flow rate:

$$x_{fA}=0.25,\ x_{fB}=0.55,\ x_{fC}=0.2 \text{ and } q_f=1.0\times10^4 \text{ cm}^3 \text{ (STP)/s}$$

Since the stage cut, defined as the fraction of the feed allowed to permeate, is θ=0.25, the permeate flow rate, q_p, is equal to 0.25×10^4 cm^3(STP)/s. The permeabilities, expressed in cm^3 (STP) cm/(s cm^2 cmHg), of components A, B, and C

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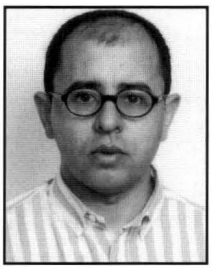

are equal to

$$P'_A = 200\times10^{-10},\ P'_B = 50\times10^{-10},\ \text{and}\ P'_C = 25\times10^{-10}.$$

This mixture is to be separated by a membrane with a thickness t=2.54×10^{-3} cm. Pressures on the feed and permeate sides are p_h=300 cmHg and p_l=30 cmHg. We will use the complete-mixing model to compute the permeate and the reject compositions as well as the membrane area. The three rate-of-permeation equations are:

$$q_p y_{pi} = \frac{P'_i}{t} A_m \left(p_h x_{Oi} - p_l y_{Pi}\right) \text{ for } i=1,2,3 \qquad (1)$$

The three material balances equations written for components A, B, and C are:

$$x_{Oi} = \frac{1}{1-\theta} x_{fi} - \frac{\theta}{1-\theta} y_{Pi} \text{ for } i=1,2,3 \qquad (2)$$

Finally, we have an additional relation that is the summation rule for mole fractions:

$$\sum_{i=1}^{3} y_{Pi} = 1 \qquad (3)$$

Equations 1 through 3 are labeled rate, matbalance, and summation, respectively. We need to enter these equations in the Mathematica notebook[2] and call *FindRoot* as follows:

```
FindRoot[{rate1, rate2, rate3,
matbalance1, matbalance2, matbalance3,
summation1}, {y_PA, 0.2}, {y_PB, 0.2}, {y_PC,
0.2}, {A_m, 10^6}, {x_OA, 0.2}, {x_OB, 0.2}-
, {x_OC,0.2}]
```

FindRoot uses different root search techniques that can be selected by the user. If one specifies only one starting value of the unknown, *FindRoot* searches for a solution using Newton methods. If the user specifies two starting values, *FindRoot* uses a variant of the secant method, which does not require the computation of derivatives. All this is handled internally by *Mathematica*, making the solution of complex systems of nonlinear algebraic equations very easy. We get the following solution for the permeate and reject compositions and the membrane area labeled A_m:

```
{y_PA → 0.455281, y_PB → 0.450286,
y_PC → 0.0944335,
A_m → 3.54176×10^6, x_OA → 0.181573,
x_OB → 0.583238, x_OC → 0.235189}
```

which is in agreement with results using a tedious iterative technique.[1]

ENRICHMENT OF AIR IN OXYGEN USING MEMBRANE PERMEATION

In this section, we present the study of the enrichment of oxygen in air using a single-stage membrane module. This problem has been treated first by Walawender and Stern[3] and later by Geankoplis.[1] The binary mixture, A (oxygen) and B (nitrogen), has an ideal separation factor, the ratio of the permeabilities of the two species, $\alpha^* = 10$. The permeability of oxygen is $P'_A = 500\times10^{-10}$ cm^3 (STP) cm/(s cm^2 cmHg). The membrane is more permeable to oxygen and has

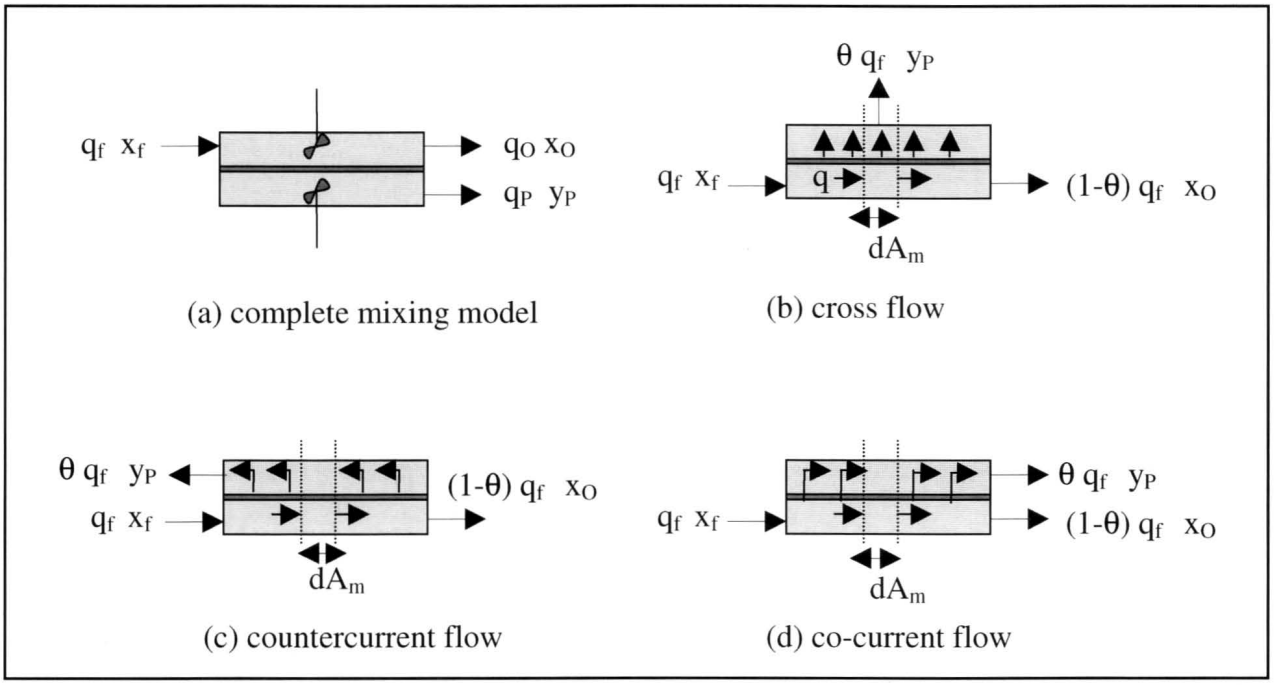

Figure 1. *Flow patterns.*

a thickness t=2.54×10^{-3} cm. The stage cut, θ, is set equal to 0.2. The values of the pressures in the feed and permeate sides chosen by Geankoplis[1] are p_h=190 cmHg and p_l=19 cmHg, which give a ratio of pressures, r, equal to 10. The feed rate and composition are given by:

x_{fA}=0.209, x_{fB}=0.791 and q_f=1.0×10^6 cm^3 (STP)/s.

The different flow patterns, shown in Figure 1 (previous page) and considered in this study, are complete mixing, cross-flow, countercurrent flow, and co-current flow. Calculations for each flow pattern will be presented in a separate subsection.

1. Complete-Mixing Case

The permeate mole fraction, y_p, is the solution of the following quadratic equation:

$$\frac{y_p}{1-y_p}=\frac{\alpha^*\left[x_O-\left(\frac{p_l}{p_h}\right)y_p\right]}{\left(1-x_O\right)-\left(\frac{p_l}{p_h}\right)\left(1-y_p\right)} \tag{4}$$

where the reject composition, x_O, is given by the mass balance:

$$x_O=\frac{x_f-\theta y_p}{1-\theta} \tag{5}$$

We also define α^* and r by $\alpha^*=P'_A/P'_B$ and $r=p_h/p_l$.

The membrane area is then obtained using Equation (6):

$$A_m=\frac{\theta q_f y_p}{\left(\frac{P'_A}{t}\right)\left(p_h x_O-p_l y_p\right)} \tag{6}$$

For our particular problem, we find the following results using Mathematica:

y_p=0.5067, x_O=0.1346, and A_{sol}=3.228×10^{8}cm^2.

These results are in agreement with those found by Geankoplis.[1]

2. Cross-Flow Case

The local permeate rates over a differential membrane area are given by

$$-ydq=\left(\frac{P'_A}{t}\right)\left(p_h x-p_l y\right)dA_m \tag{7}$$

$$-\left(1-y\right)dq=\left(\frac{P'_B}{t}\right)\left(p_h\left(1-x\right)-p_l\left(1-y\right)\right)dA_m \tag{8}$$

In addition, we can derive Equation (9) from total and component mass balances:

$$ydq=d(qx) \tag{9}$$

These three governing equations are solved simultaneously using the Mathematica built-in function called *NDSolve*. The following boundary conditions are used:

$$q\big|_{A_m=0}=q_f,\ x\big|_{A_m=0}=x_{fA}\ \text{and}\ y\big|_{A_m=0}=y_{Pi}\ .$$

where y_{Pi} is obtained by solving the quadratic equation

$$\frac{y_{Pi}}{1-y_{Pi}}=\frac{\alpha^*\left[x_{fA}-\left(\frac{p_l}{p_h}\right)y_{Pi}\right]}{\left(1-x_{fA}\right)-\left(\frac{p_l}{p_h}\right)\left(1-y_{Pi}\right)} \tag{10}$$

The command used in the notebook to solve the system of ODEs is:

```
myODEsoln[Ω_] :=:

NDSolve[{y[A_m] D[q[A_m], {A_m, 1}]==
D[q[A_m] x[A_m], {A_m, 1}],

-y[A_m] D[q[A_m], {A_m,1}]== P'_A/t (p_h x[A_m]
- p_l y[A_m]),

-(1- y[A_m]) D[q[A_m], {A_m,1}]==

P'_B/t+(p_h(1- x[A_m]) - p_l(1- y[A_m])), x[0]
== x_f,

y[0] == y_Pi, q[0] == q_f, {x[A_m],
y[A_m], q[A_m]}, {A_m, 0, Ω}]
```

We use *FindRoot* to get the total membrane area. In fact, we must satisfy the following condition: θ=0.2 where the stage cut, θ, is given by $\theta=(q_f-q|_{end})/q_f$.

The Mathematica command is written as follows:

```
qend[Ω_?NumericQ] : =Flatten[(q[A_m] /.
myODEsoln[Ω])/.A_m → Ω]

A_sol = FindRoot[(q_f- qend[Ω])/q_f==θ,
{Ω,2 10^8,3 10^8}, MaxIterations→1000];
```

The final result is a membrane area and a reject composition equal to: A_{sol}=2.899×10^8 cm^2 and x_O=0.1190. A component balance, $\theta y_p+(1-\theta)x_O=x_{fA}$, can be used to obtain the permeate mole fraction and we find that y_p=0.5688. Our approach gives similar results as those given by Geankoplis[1] but is far less tedious and more accurate. We can check our results by integrating $y(A_m)$ for A_m varying from 0 to A_{sol}, achieved with the command:

```
Integrate[First[y[A_m]/.myODEsoln[Ω/
.A_sol]] /. A_m→area,

{area, 0, Ω /.A_sol}]/Ω/.A_sol
```

We get y_p=0.5634, a value in agreement with the previous result. Since numerical integration is used, the later value of

y_p is less exact. In Figure 2, we plot the mole fraction in the permeate and feed sides in the membrane module. Similar figures can be easily drawn for the other flow patterns using the graphical capabilities of Mathematica. Figure 2 clearly shows that the oxygen mole fraction in the feed side of the module varies from the inlet value, x_f=0.209, to the reject value, x_O=0.1190.

3. Countercurrent-Flow Case

The flow diagram for the countercurrent-flow pattern is shown in Figure 1. Both streams are in plug flow. The two governing equations have been derived by Oishi, *et al.*,[4] and Walawender and Stern[3]:

$$\left(\frac{q_O t}{p_l P'_B}\right)\frac{dx}{dA_m}=\left(\frac{x-y}{y-x_O}\right)\left\{(1-x)\alpha^*(rx-y)-x\left[r(1-x)-(1-y)\right]\right\} \tag{11}$$

$$\left(\frac{q_O t}{p_l P'_B}\right)\frac{dy}{dA_m}=\left(\frac{y-x}{x-x_O}\right)\left\{(1-y)\alpha^*(rx-y)-y\left[r(1-x)-(1-y)\right]\right\} \tag{12}$$

where $q_O=(1-\theta)q_f$. The following boundary conditions

$$x\big|_{A_m=0}=x_O \text{ and } y\big|_{A_m=0}=y_i,$$

are used where y_i is the solution of the quadratic equation:

$$\frac{y_i}{1-y_i}=\frac{\alpha^*\left[x_O-\left(\frac{p_l}{p_h}\right)y_i\right]}{(1-x_O)-\left(\frac{p_l}{p_h}\right)(1-y_i)} \tag{13}$$

We use L'Hopital's rule to compute the derivatives at A_m=0 because they become indeterminate when x=x_O. This is performed as follows:

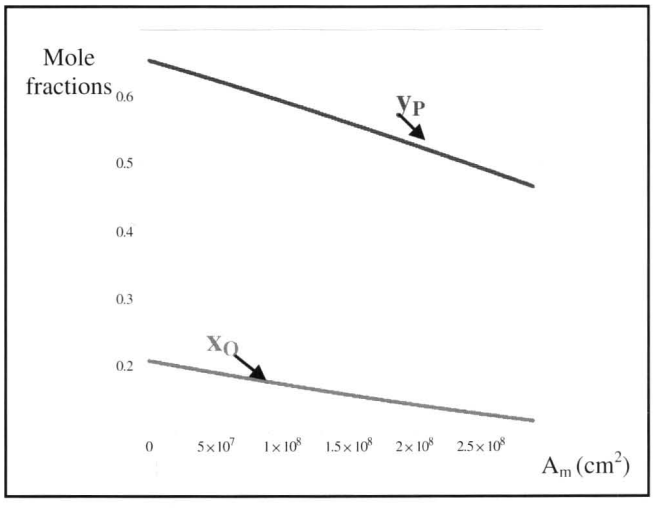

Figure 2. *Mole fractions of reject and permeate.*

$$\left(\frac{dy}{dA_m}\right)_{A_m=0}=\frac{(x_O-y_i)r\left[\alpha^*-y_i(\alpha^*-1)\right]}{\left(\frac{q_O t}{p_l P'_B}\right)-\frac{\left\{(x_O-y_i)\left[(\alpha^*-1)(2y_i-rx_O-1)-r\right]\right\}}{\left(\frac{dx}{dA_m}\right)_{A_m=0}}} \tag{14}$$

$$\left(\frac{dx}{dA_m}\right)_{A_m=0}=\frac{1}{\left(\frac{q_O t}{p_l P'_B}\right)}\left[\frac{\alpha^*(rx_O-y_i)(x_O-y_i)}{y_i}\right] \tag{15}$$

These two differential equations can be solved simultaneously using *NDSolve*. We enter the equations using an If statement to take into account the derivative expression when $A_m \to 0$:

```
eq1[a_] :=D[x[Am], {Am, 1}] ==
If[Am == 0,
Evaluate[
(pl P'B)/(qO t) α (xo ph/ pl - yi)(xo- yi)/
yi /.
t-> 2.54 10^-3/. ph -> 190 /. pl -> 19/.
α -> 10/.
P'B -> 50 10^-10/. qO -> 8 10^5 /
.xo→a],
Evaluate[
(pl P'B)/(qO t)(x[Am] - y[Am])/ (y[Am] -
xo)
((1- x[Am]) α (ph/pl x[Am] - y[Am])-
x[Am] (ph/pl (1-x[Am])-(1-y[Am])))/.
t-> 2.54 10^-3/. ph -> 190 /. pl -> 19/.
α -> 10/.
P'B -> 50 10^-10/. qO -> 8 10^5 /
.xo→a]]
```

Since the value of the reject mole fraction, x_O, and the total area, A_m, are unknown, we use *FindRoot* to solve for these two unknowns so that the mole fraction of oxygen in the feed is 0.209 and that the material balance for component A is verified:

$$x\big|_{A_{sol}}=x_{fA} \text{ and } \theta y_P\big|_{A_{sol}}+(1-\theta)x_O=x_{Af}$$

Following the treatment of Walawender and Stern,[3] we set the area equal to zero at the outlet of the gas separation module. Thus, the sign of the membrane area obtained using this approach is negative and must be reversed. We get the following results: $A_{sol}=2.859\times10^8$ cm^2, y_p=0.5763, and x_O=0.1171. We find a smaller membrane area and reject mole

fraction and a higher permeate composition.

4. Co-Current-Flow Case

The governing equations[3] are derived in a similar fashion to the preceding case.

$$\left(\frac{q_f t}{p_l P_B^{'}}\right)\frac{dy}{dA_m}=\left(\frac{x-y}{x-x_f}\right)\left\{(1-y)\alpha^*(rx-y)-y\left[r(1-x)-(1-y)\right]\right\} \tag{16}$$

$$\left(\frac{q_f t}{p_l P_B^{'}}\right)\frac{dx}{dA_m}=\left(\frac{x-y}{y-x_f}\right)\left\{(1-x)\alpha^*(rx-y)-x\left[r(1-x)-(1-y)\right]\right\} \tag{17}$$

The following boundary conditions must be used: $x|_{A_m=0}=x_{Af}$ and $y|_{A_m=0}=y_i$. The value of y_i is a solution of the following quadratic equation:

$$\frac{y_i}{1-y_i}=\frac{\alpha^*\left[x_f-\left(\frac{p_l}{p_h}\right)y_i\right]}{(1-x_f)-\left(\frac{p_l}{p_h}\right)(1-y_i)} \tag{18}$$

Inspection of Equation (16) shows that the derivatives are indeterminate when $A_m \to 0$. We use L'Hopital's rule to get expressions for the derivatives at A_m=0 as follows:

$$\left(\frac{dy}{dA_m}\right)_{A_m=0}=\frac{(x_f-y_i)r\left[\alpha^*-y_i(\alpha^*-1)\right]}{\left(\frac{q_f t}{p_l P_B^{'}}\right)-\frac{\left\{(x_f-y_i)\left[(\alpha^*-1)(2y_i-rx_f-1)-r\right]\right\}}{\left(\frac{dx}{dA_m}\right)_{A_m=0}}} \tag{19}$$

$$\left(\frac{dx}{dA_m}\right)_{A_m=0}=\frac{1}{\left(\frac{q_f t}{p_l P_B^{'}}\right)}\left[\frac{\alpha^*(rx_f-y_i)(x_f-y_i)}{y_i}\right] \tag{20}$$

The value of the total membrane area is found using *FindRoot* to satisfy the material balance for oxygen: $\theta y_p|_{A_{sol}}+(1-\theta)x_O=x_{Af}$. The membrane area, permeate composition, and reject mole fraction are equal to: $A_{sol}=2.955\times10^8$ cm^2, y_p=0.5584 and x_O=0.1216.

5. Comparing the Different Flow Patterns

The membrane areas are equal within 10%. The smallest membrane area is obtained using the countercurrent flow pattern. The countercurrent case requires a smaller membrane area because the driving force for permeation (the composition difference between permeate and feed sides) is higher than in the other flow patterns. The complete-mixing model gives the highest membrane area. The reject mole fractions and the permeate compositions obtained for the four cases studied show similar trends. The most efficient flow pattern is the countercurrent mode. In fact, the order of efficiency is the following: countercurrent flow > cross-flow > co-current flow > complete-mixing model. Reducing membrane area has a major impact on capital investment costs. Thus, the countercurrent flow pattern is the optimal design choice. Other relevant parameters for reducing membrane area are thickness and permeability of the membrane and operating pressure, which will affect operating costs as well.

CONCLUSIONS

In this study, we showed how simple Mathematica commands[2] can be used to solve problems that required tedious iterative techniques or complicated programming skills. We present the solutions of two problems proposed by Professor Geankoplis.[1] We extend this author's work to the countercurrent and co-current flow patterns. These problems are given to the junior and senior students of the National Institute of Applied Sciences in Tunis as small research projects. The students excel in these type of problems despite the fact that they do not have prior knowledge of Mathematica.

NOMENCLATURE

A_m	membrane area
$P_i^{'}$	permeability of component i
p_h	feed side pressure
p_l	permeate side pressure
q_f	feed flow rate
q_p	permeate flow rate
q_o	reject flow rate
t	membrane thickness
r	ratio of pressures of feed and permeate sides
x_{fi}	feed mole fraction of component i
x_O	reject mole fraction
y_P	permeate mole fraction
α^*	separation factor
θ	stage cut

REFERENCES

1. Geankoplis, C.J., *Transport Processes and Unit Operations*, 3rd Ed., Prentice Hall, Upper Saddle River, NJ (1993) (example 13.5-1, page 771 and example 13.4-2, page 767)
2. <http://library.wolfram.com/infocenter/search/?search_results=1;search_person_id=1536>
3. Walawender, W.P., and S.A. Stern, *Separation Science*, 7 **5**, 553-584 (1972)
4. Oishi, J., Y. Matsumura, K. Higashi, and C. Ike, *J. At. Energy Soc. Japan*, **3**, 923 (1961) ❐