Membrane Separation Processes

Membrane separations represent a new type of unit operation. The membrane acts as a semipermeable barrier and separation occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gas phases, or a liquid and a gas phase. The two fluid phases are usually miscible and the membrane barrier prevents actual, ordinary hydrodynamic flow.

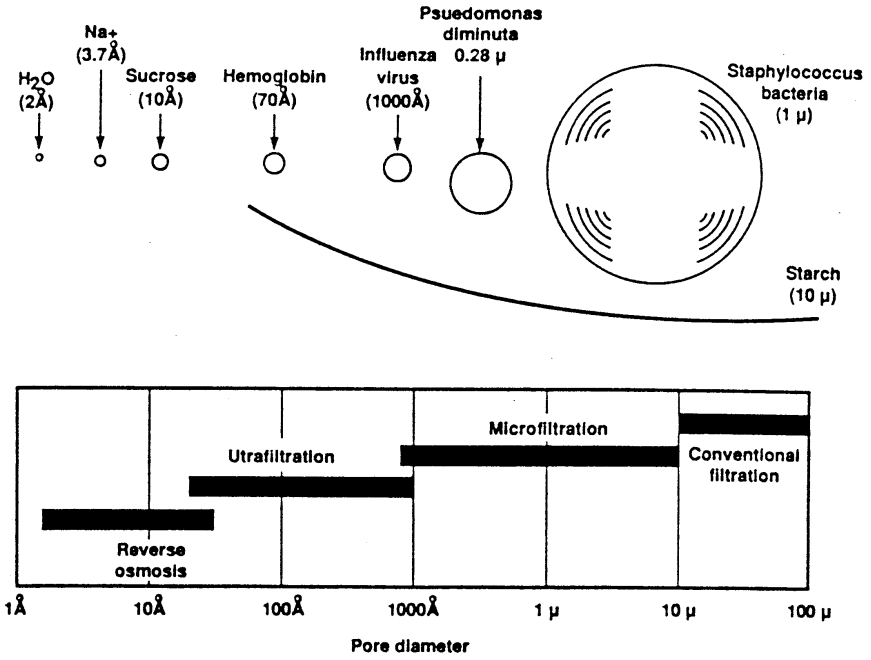
References:

C.J. Geankoplis, "*Transport Processes and Unit Operations*", 3rd ed., Prentice Hall, Englewood Cliffs, New Jersey, 1993. *(Chapter 13)*

W.L. McCabe, J.C. Smith, P. Harriott, *"Unit Operations of Chemical Engineering*", 5th ed., McGraw-Hill, New York, 1993. *(Chapter 26)*

1. Classification of membrane processes

- Porous membrane
  - ♣ Gas diffusion:
    The rates of gas diffusion depend on the pore sizes and the molecular weights. We may have molecular, transition, and Knudsen diffusion regions depending on the relative sizes of pore and gas molecule.
  - ♣ Microfiltration (MF):
    This refers to membranes that have pore diameters from 0.1 to 10 μm. It is used to filter suspended particulates, bacteria or large colloids from solution.
  - ♣ Ultrafiltration (UF):
    This refers to membranes having pore diameters in the range 20-1000 $\mathring{A}$. It can be used to filter dissolved macromolecules, such as proteins and polymers, from solution.
  - ♣ Reverse osmosis (RO):
    The membrane pores are in the range of 5-20 $\mathring{A}$ in diameter, which are within the range of the thermal motion of the polymer chains.
  - ♣ Dialysis



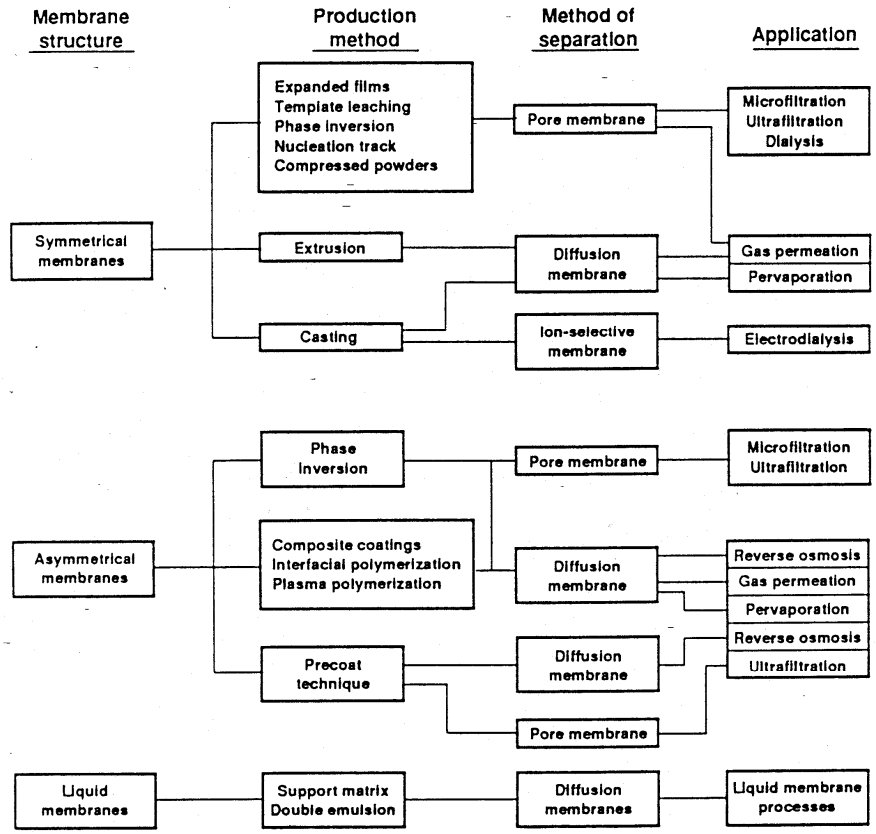
1. Reverse osmosis, ultrafiltration, microfiltration and conventional filtration are all related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist. Transport in this case occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic.

Figure 1.

• Tight (nonporous, or dense) membrane

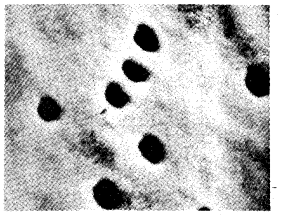
Here the permeants are sorbed into the membrane material under the influence of their thermodynamic potential and pass it as a result of a driving force exerted:

- ♣ Gradient of vapor pressure
  pervaporation (feed is liquid)
  vapor permeation (feed is vapor)
- ♣ Pressure gradient
  gas permeation (feed & permeant are gases)
  reverse osmosis (feed & permeant are liquids)
- ♣ Temperature gradient
  thermoosmosis
- ♣ Concentration gradient
  dialysis (osmosis, liquid permeation)
  pertraction
- ♣ Gradient in electric potential
  electrodialysis (ion-selective membrane)

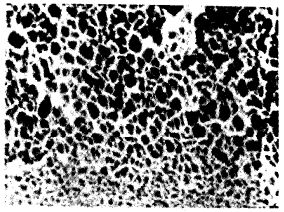


Membrane classification.

Symmetrical Membranes

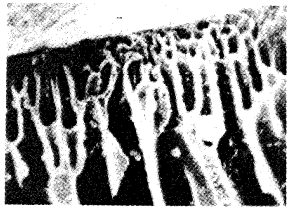


Nucleation Track Membrane

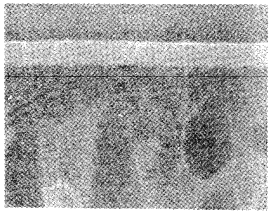


Microporous Phase-Inversion Membrane

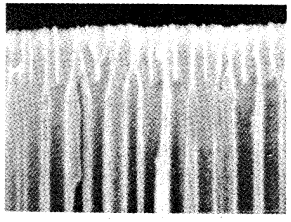
Asymmetrical Membranes



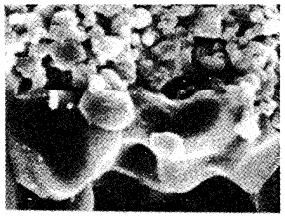
Loeb-Sourirajan Phase-Inversion Membrane



Silicone-Rubber Coated Composite Membrane



Electrolytically-Deposited Membrane



Multilayer Ceramic Membrane

Types of membrane structures.

2. Dialysis (liquid permeation)

In this case the small solutes in one liquid phase diffuse through a porous membrane to the second liquid phase where the permeants are diluted by means of a so-called sweeping solvent. The driving force is a concentration gradient so the flux rates are low. If the boiling point of the permeants is much lower than that of the sweeping liquid, the permeants can be separated by flashing from the sweeping liquid, the dialysis process is called pertraction.

In practice dialysis is used to separate species that differ appreciably in size, which have a large difference in diffusion rates. Applications include recovery of sodium hydroxide in cellulose processing, recovery of acids from metallurgical liquors, removal of products from a culture solution in fermentation, and reduction of alcohol content of beer.

2.1 Series resistances in membrane processes

In dialysis, the solute molecules must first be transported or diffuse through the liquid film of the first liquid phase on one side of the solid membrane, through the membrane itself, and then through the film of the second liquid phase. This is shown in Figure 2, where c_1 is the bulk liquid phase concentration of the diffusing solute A in kg mol A/m^3, c_{1i} is the concentration of A in the fluid just adjacent to the solid, and c_{1iS} is the concentration of A in the solid at the surface and is in equilibrium with c_{1i}. The mass transfer coefficients are k_{c1} and k_{c2} in m/s. The equilibrium distribution coefficient K' is defined as:

$$K' = \frac{c_S}{c_L} = \frac{c_{1iS}}{c_{1i}} = \frac{c_{2iS}}{c_{2i}} \qquad (1)$$

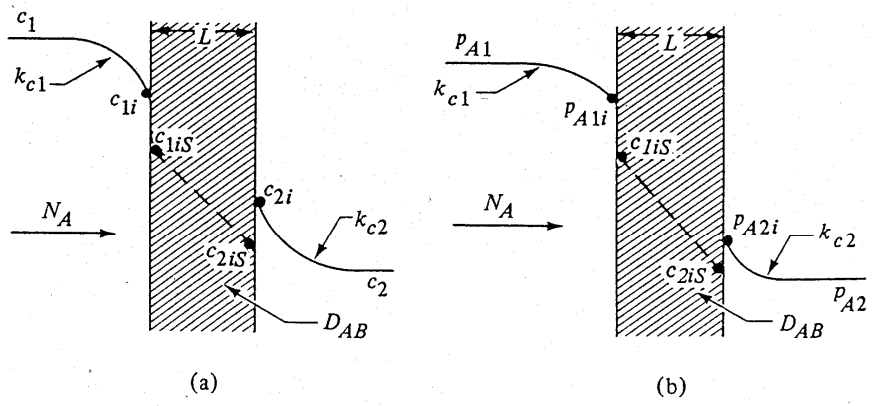


FIGURE 2 *Concentration profiles for membrane processes: (a) two liquid films and a solid, (b) two gas films and a solid.*

The flux equations through each phase are all equal to each other at steady state:

$$N_A = k_{c1}(c_1 - c_{1i}) = \frac{D_{AB}}{L}(c_{1iS} - c_{2iS}) = k_{c2}(c_{2i} - c_2) \quad (2)$$

Substituting Eq. (1) into Eq. (2),

$$N_A = k_{c1}(c_1 - c_{1i}) = \frac{D_{AB}K'}{L}(c_{1i} - c_{2i}) = p_M(c_{1i} - c_{2i}) = k_{c2}(c_{2i} - c_2) \quad (3)$$

$$p_M = \frac{D_{AB}K'}{L} \quad (4)$$

where p_M is the permeability in the solid in m/s, L is the thickness in m, and D_{AB} is the diffusivity of A in the solid in m^2/s. Instead of determining D_{AB} and K' in two separate experiments, it is more convenient to determine p_M in one experiment. The concentration differences can be obtained from Eq. (3):

$$c_1 - c_{1i} = \frac{N_A}{k_{c1}} \qquad c_{1i} - c_{2i} = \frac{N_A}{p_M} \qquad c_{2i} - c_2 = \frac{N_A}{k_{c2}} \quad (5)$$

By adding three equations, the internal concentrations drop out, the final equation is

$$N_A = \frac{c_1 - c_2}{1/k_{c1} + 1/p_M + 1/k_{c2}} \quad (6)$$

The denominator can be considered as the inverse of overall mass transfer coefficient. In some cases, the resistances in the two liquid films are quite small

compared to that of the membrane resistance, which controls the permeation rate.

Example 1: Membrane diffusion and liquid film resistances

A liquid containing dilute solute A at a concentration c_1=0.030 kg mol/m^3 is flowing rapidly by a membrane of thickness L=3.0x10^{-5} m. The distribution coefficient K'=1.5 and D_{AB}=7.0x10^{-11} m^2/s in the membrane. The solute diffuses through the membrane and its concentration on the other side is c_2=0.0050 kg mol/m^3. The mass transfer coefficient k_{c1} is large and can be considered as infinite and k_{c2} =2.02x10^{-5} m/s.

(a) Derive the equation to calculate the steady-state flux N_A and make a sketch.

(b) Calculate the flux and the concentrations at the membrane interfaces.

Solution: For part (a) the sketch is shown in Fig. 3. Note that the concentration on the left side is flat ($k_{c1}=\infty$) and $c_1 = c_{1i}$. The derivation is the same as for Eq. (6) but $1/k_{c1} = 0$ to give

$$N_A = \frac{c_1 - c_2}{1/p_M + 1/k_{c2}} \quad (7)$$

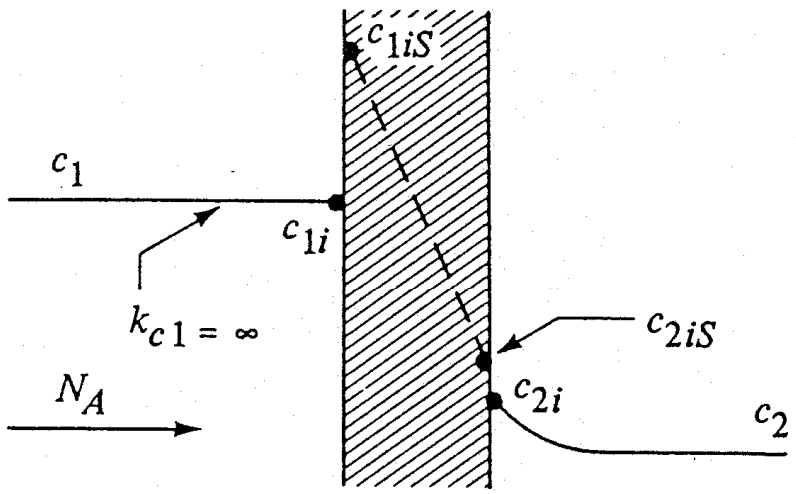


FIGURE 3 *Concentrations for Example 13.2-1.*

For part (b),

$$p_M = \frac{D_{AB}K'}{L} = \frac{7.0\times10^{-11}(1.5)}{3.0\times10^{-5}} = 3.5\times10^{-6}\ \text{m/s}$$

$$N_A = \frac{c_1 - c_2}{1/p_M + 1/k_{c2}} = \frac{0.030 - 0.005}{1/3.5\times10^{-6} + 1/2.02\times10^{-5}}$$

$$= 7.458\times10^{-8}\ \text{kg mol/s m}^2$$

To calculate c_{2i},

$$N_A = 7.458\times10^{-8} = k_{c2}(c_{2i} - c_2) = 2.02\times10^{-5}(c_{2i} - 0.005)$$

Solving $c_{2i} = 0.00869$ kg mol/m^3.

$$c_{2iS} = K'c_{2i} = 1.5\times0.00869 = 0.01304\ \text{kg mol/m}^3$$

$$c_{1iS} = K'c_{1i} = K'c_1 = 1.5\times0.03 = 0.045\ \text{kg mol/m}^3$$

3. Gas permeation

3.1 Series resistances in membrane processes

Similar equations to dialysis can be written for gas permeation. The equilibrium relation between the solid and gas phases is given by

$$H = \frac{S}{22.414} = \frac{c_S}{p_A} = \frac{c_{1iS}}{p_{A1i}} = \frac{c_{2iS}}{p_{A2i}} \qquad (8)$$

where S is the solubility of A in m^3 (STP)/atm m^3 solid, and H is the equilibrium relation in kg mol/m^3 atm. This is similar to Henry's law. The flux equations in each phase are as follows:

$$N_A = \frac{k_{c1}}{RT}(p_{A1} - p_{A1i}) = \frac{D_{AB}}{L}(c_{1iS} - c_{2iS})$$
$$= \frac{D_{AB}H}{L}(p_{A1i} - p_{A2i}) = \frac{k_{c2}}{RT}(p_{A2i} - p_{A2}) \qquad (9)$$

The permeability P_m in kg mol/s m atm is given by

$$P_m = D_{AB}H = \frac{D_{AB}S}{22.414} \qquad (10)$$

Eliminating the interfacial concentrations as before,

$$N_A = \frac{p_{A1} - p_{A2}}{1/(k_{c1}/RT) + 1/(p_m/L) + 1/(k_{c2}/RT)} \qquad (11)$$

Note that $k_{G1} = k_{c1}/RT$. An example of gas permeation in a membrane is use of a polymeric membrane as an oxygenator for a heart-lung machine. Pure O_2 is on one side of a thin membrane and blood is on the other side. Oxygen diffuses through the membrane into the blood and CO_2 diffuses in a reverse direction into the gas stream.

3.2 Types of membranes and permeabilities for gas separation

The permeation flux is inversely proportional to the thickness of the membrane. So if the membrane is thick (100 μm), as used in the early stage to prevent any tiny holes which reduced the separation, the flux is low. Some newer asymmetric membranes include a very thin but dense skin on one side of the membrane supported by a porous substructure. The dense skin has a thickness of about 1000 Å and the porous support thickness is about 25-100 μm. The flux is thousands of times higher than the 100-μm-thick original membranes. Some typical materials of present membranes are a composite of polysulfone coated with silicon rubber, cellulose acetate and modified cellulose acetate, aromatic polyamides or aromatic polyimides, and silicon-polycarbonate copolymer on a porous support.

Experiments are necessary to determine the permeabilities of gases in membranes. Some typical data are listed in Table 1. In a given membrane the permeabilities of various gases may differ significantly.

For the effect of temperature T in K, the $\ln P_A'$ increases with T following approximately a linear function of 1/T. However, operation at high temperatures can often degrade the membranes. When a mixture of gases is present, the permeability of an individual component may be reduced by up to 10%. Hence, when using a mixture of gases, experimental data should be obtained to determine if there is any interaction between the gases. The presence of water vapor can also have similar effects.

TABLE 1 *Permeabilities of Various Gases in Membranes*

Material	*Temp. (°C)*	*Permeability, P'_A, $\frac{cm^3(STP)\cdot cm}{s\cdot cm^2\cdot cm\ Hg}\times 10^{10}$*						
		He	*H_2*	*CH_4*	*CO_2*	*O_2*	*N_2*	*Ref.*
Silicone rubber	25	300	550	800	2700	500	250	(S2)
Natural rubber	25	31	49	30	131	24	8.1	(S2)
Polycarbonate (Lexane)	25–30	15	12		5.6,10	1.4		(S2)
Nylon 66	25	1.0			0.17	0.034	0.008	(S2)
Polyester (Permasep)	—		1.65	0.035	0.31		0.031	(H1)
Silicone–polycarbonate copolymer (57% silicone)	25		210		970	160	70	(W2)
Teflon FEP	30	62		1.4			2.5	(S1)
Ethyl cellulose	30	35.7	49.2	7.47	47.5	11.2	3.29	(W3)
Polystyrene	30	40.8	56.0	2.72	23.3	7.47	2.55	(W3)

3.3 Types of equipment for gas permeation

3.3.1 Flat membranes. These are mainly used to experimentally characterize the permeability of the membrane. The modules are easy to fabricate and use and the areas of the membranes are well defined. In some cases modules are stacked together like a multilayer sandwich or plate-and-frame filter press. The major drawback of this type is the very small membrane area per unit separator volume.

3.3.2 Spiral-wound membranes. This configuration increases markedly the membrane area per unit separator volume up to 328 m^2/ m^3 and decreases the pressure drop. The assembly consists of a sandwich of four sheets wrapped around a central core of a perforated collecting tube. The four sheets consists of a top sheet of an open separator grid for the feed channel, a membrane, a porous felt backing for the permeate channel, and another membrane as shown in Fig. 4. The spiral-wound element is 100 to 200 mm in diameter and is about 1 to 1.5 m long in the axial direction. The flat sheets before rolling are about 1 to 1.5 m by 2 to 2.5 m. The space between the membranes (open grid for feed) is about 1 mm and the thickness of the porous backing (for permeate) is about 0.2 mm.

The whole spiral-wound element is located inside a metal shell. The feed gas enters at the left end of the shell, enters the feed channel, and flows through this channel in the axial direction of the spiral to the right end where the exit residue gas leaves. The feed stream permeates perpendicularly through the membrane. This permeate then flows through the permeate channel toward the perforated collecting tube, where it leaves the apparatus at one end.

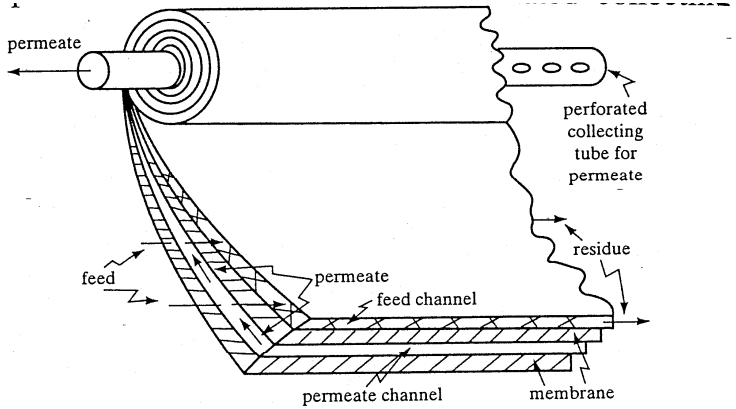


FIGURE 4 *Spiral-wound elements and assembly.*

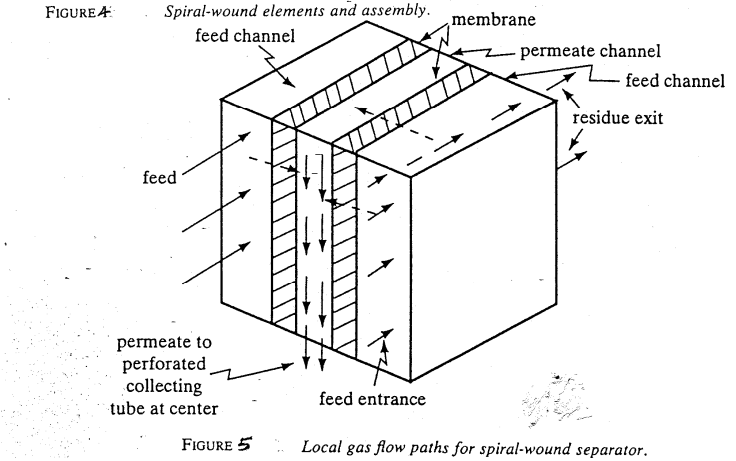


FIGURE 5 *Local gas flow paths for spiral-wound separator.*

3.3.3 Hollow-fibre membranes. The membranes are in the shape of very small diameter hollow fibres. The inside diameter of the fibres is in the range of 100 to 500 μm and the outside 200 to 1000 μm with the length up to 3 to 5 m. The module resembles a shell-and-tube heat exchanger. Thousands of fine tubes are bound together at each end into a tube sheet that is surrounded by a metal shell having a diameter of 0.1 to 0.2 m, so that the membrane area per unit volume is up to 10000 m^2/ m^3.

The high pressure feed enters into the shell side at one end and leaves at the other end. The hollow fibres are closed at one end of the tube bundles. The permeate gas inside the fibres flow countercurrently to the shell-side flow and is collected in a chamber where the open ends of the fibres terminate.

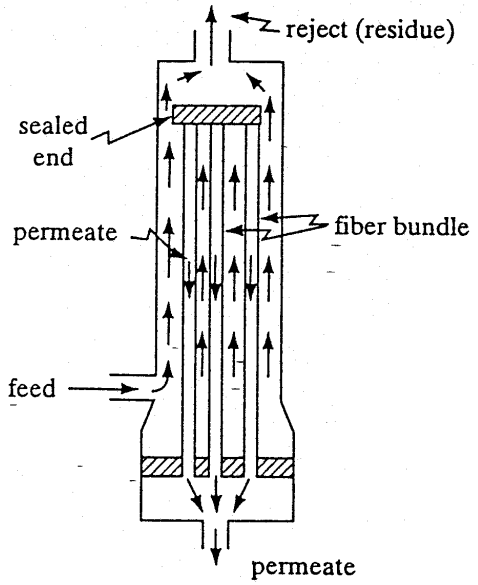


FIGURE 6 *Hollow-fiber separator assembly.*

3.4 Types of flow in gas permeation

Because of the very high diffusion coefficient in gases, concentration gradients in the gas phase in the direction normal to the surface of the membrane are quite small. Hence, gas film resistance compared to the membrane resistance can be ignored.

If the gas stream is flowing parallel to the membrane in plug flow, a concentration gradient occurs in this direction. Hence, several cases can occur in the operation of a membrane module. Both permeate and feed sides can be operated completely mixed or in plug flow. Countercurrent or cocurrent flow can be used when both sides are in plug flow. This is summarized in Figure 7.

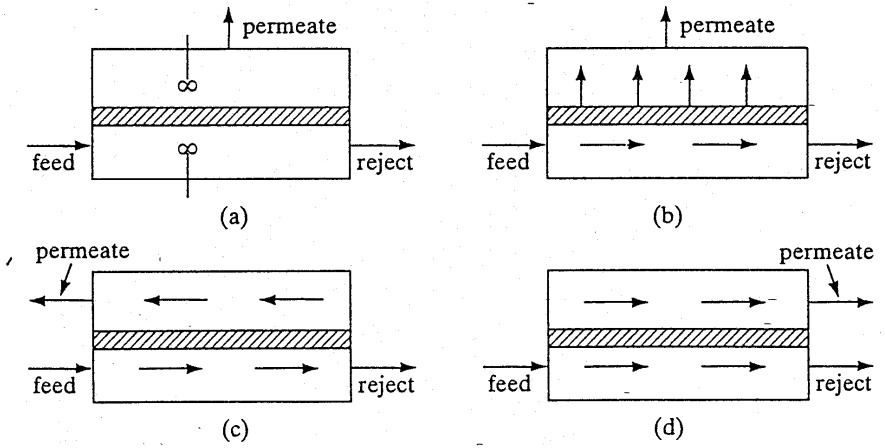


FIGURE 7 *Ideal flow patterns in a membrane separator for gases: (a) complete mixing, (b) cross-flow, (c) countercurrent flow, (d) cocurrent flow.*

4. Complete-mixing model for gas separation

4.1 Basic equations used

A detailed diagram is shown in Fig. 8 for complete mixing. The overall material balance is

$$q_f = q_0 + q_p \quad (12)$$

where q_f is the total feed flow rate in cm^3 (STP)/s; q_0 is outlet reject flow rate in the same unit; and q_p is outlet permeate flow rate, cm^3 (STP)/s. The cut or fraction of feed permeated, θ, is given as: $\theta = \frac{q_p}{q_f}$ (13)

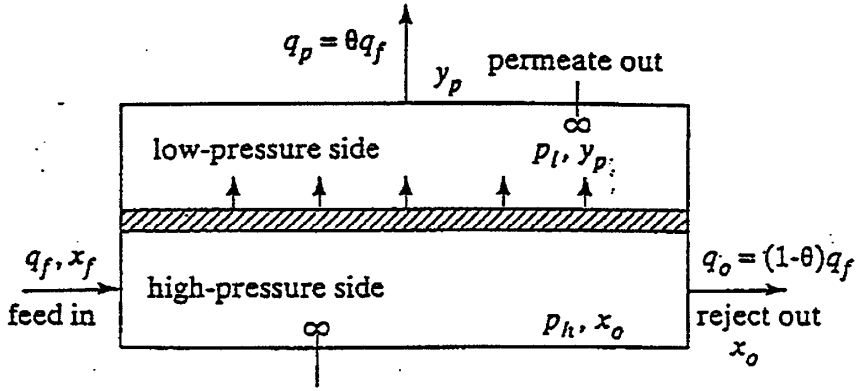


FIGURE *Process flow for complete mixing case.*

The rate of diffusion or permeation of species A (in a binary of A and B) is given below

$$\frac{q_A}{A_m} = \frac{q_p y_p}{A_m} = \left(\frac{P_A'}{t}\right)\left(p_h x_0 - p_l y_p\right) \quad (14)$$

where P_A' is the permeability of A in the membrane, cm^3 (STP) cm/(s cm^2 cm Hg); q_A is the flow rate of

A in permeate, cm^3 (STP)/s; A_m is membrane area, cm^2; t is membrane thickness, cm; p_h is the total pressure in the high pressure (feed) side, cm Hg; p_l is the total pressure in the low pressure or permeate side, cm Hg; x_0 is the mole fraction of A in the reject side; and y_p is the mole fraction of A in the permeate. Note that $p_h x_0$ is the partial pressure of A in the reject gas phase.

A similar equation can be written for component B:

$$\frac{q_B}{A_m} = \frac{q_p(1-y_p)}{A_m} = \left(\frac{P_B'}{t}\right)\left(p_h(1-x_0) - p_l(1-y_p)\right) \quad (15)$$

Dividing Eq. (14) by (15) gives

$$\frac{y_p}{1-y_p} = \frac{\alpha^*\left[x_0 - (p_l/p_h)y_p\right]}{(1-x_0) - (p_l/p_h)(1-y_p)} \quad (16)$$

This equation relates y_p, the permeate composition, to x_0, the reject composition, and the ideal separation factor α^* is defined as

$$\alpha^* = \frac{P_A'}{P_B'} \quad (17)$$

Making an overall mass balance on component A

$$q_f x_f = q_0 x_0 + q_p y_p \quad (18)$$

Dividing by q_f and solving for the exit compositions,

$$x_0 = \frac{x_f - \theta y_p}{(1-\theta)} \quad \text{or} \quad y_p = \frac{x_f - x_0(1-\theta)}{\theta} \quad (19)$$

$$A_m = \frac{\theta q_f y_p}{\left(P_A'/t\right)\left(p_h x_0 - p_l y_p\right)} \quad (20)$$

4.2 Solution of equations for the design of complete-mixing case

For the design of a complete-mixing model, there are seven variables, x_f, x_0, y_p, θ, α^*, p_l/p_h, and A_m, four of which are independent variables. Let us consider two common cases.

Case 1. x_f, x_0, α^*, and p_l/p_h are given and y_p, θ, and A_m are to be determined by solution of the equations. Eq. (16) can be rearranged as

$$a(y_p)^2 + by_p + c = 0 \qquad (21)$$

where

$$a = 1 - \alpha^*$$

$$b = \frac{p_h}{p_l}(1 - x_0) - 1 + \alpha^* \frac{p_h}{p_l} x_0 + \alpha^* \qquad (22)$$

$$c = -\alpha^* \frac{p_h}{p_l} x_0$$

and the solution is

$$y_p = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \qquad (23)$$

Example 2. Design of membrane unit for complete mixing

A membrane is to be used to separate a gaseous mixture of A and B whose feed flow rate is $q_f = 1\text{x}10^4$ cm^3(STP)/s and feed composition of A is $x_f = 0.50$ mole fraction. The desired composition of the reject is $x_0 = 0.25$. The membrane thickness $t = 2.54\text{x}10^{-3}$ cm, the pressure on the feed side is $p_h = 80$ cm Hg and on the permeate side is $p_l = 20$ cm Hg. The permeabilities are $P_A' = 50\text{x}10^{-10}$ cm^3(STP)/(s cm^3 cm Hg) and $P_B = 5\text{x}10^{-10}$. Assuming the complete-mixing model, calculate the permeate composition, y_p, the fraction permeated, θ, and the membrane area, A_m.

Solution:

$$\alpha^* = \frac{P_A'}{P_B'} = \frac{50 \times 10^{-10}}{5 \times 10^{-10}} = 10$$

$$a = 1 - \alpha^* = 1 - 10 = -9$$

$$b = \frac{p_h}{p_l}(1 - x_0) - 1 + \alpha^* \frac{p_h}{p_l} x_0 + \alpha^*$$

$$= \frac{80}{20}(1 - 0.25) - 1 + 10\left(\frac{80}{20}\right)(0.25) + 10 = 22$$

$$c = -\alpha^* \frac{p_h}{p_l} x_0 = -10\left(\frac{80}{20}\right)(0.25) = -10$$

$$y_p = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{-22 + \sqrt{22^2 - 4(-9)(-10)}}{2(-9)} = 0.604$$

$$x_0 = \frac{x_f - \theta y_p}{1-\theta} \qquad 0.25 = \frac{0.50 - \theta(0.604)}{1-\theta}$$

Solving $\theta = 0.706$

$$A_m = \frac{\theta q_f y_p}{(P_A'/\ t)\left(p_h x_0 - p_l y_p\right)}$$

$$= \frac{0.706(1\times10^4)(0.604)}{\left[50\times10^{-10}\ /\left(2.54\times10^{-3}\right)\right](80\times0.25 - 20\times0.604)}$$

$$= 2.735\times10^8\ \text{cm}^2 = 27350\ \text{m}^2$$

Case 2. x_f, θ, α^*, and p_l/p_h are given and y_p, x_0, and A_m are to be determined. Eq. (19) is substituted into Eq. (16) and the result in the form of $a_1(y_p)^2 + b_1 y_p + c_1 = 0$ and $y_p = \dfrac{-b_1 + \sqrt{b_1^2 - 4a_1c_1}}{2a_1}$ is

$$a_1 = \theta + \frac{p_l}{p_h} - \frac{p_l}{p_h}\theta - \alpha^*\theta - \alpha^*\frac{p_l}{p_h} + \alpha^*\frac{p_l}{p_h}\theta$$

$$b_1 = 1 - \theta - x_f - \frac{p_l}{p_h} + \frac{p_l}{p_h}\theta + \alpha^*\theta + \alpha^*\frac{p_l}{p_h} - \alpha^*\frac{p_l}{p_h}\theta + \alpha^* x_f$$

$$c_1 = -\alpha^* x_f$$

4.3 Minimum concentration of reject stream

If all of the feed is permeated, then $\theta = 1$ and the feed composition $x_f = y_p$. For all values of $\theta < 1$, the permeate concentration $y_p > x_f$. Rearranging Eq. (16) to give

$$x_0 = \frac{y_p\left[1 + \left(\alpha^* - 1\right)\frac{p_l}{p_h}\left(1 - y_p\right)\right]}{\alpha^*\left(1 - y_p\right) + y_p} \qquad (24)$$

which means that x_0 is a monotonic increasing function with y_p. When y_p is at its minimum value of x_f, the reject composition have its minimum as

$$x_{0M} = \frac{x_f\left[1 + \left(\alpha^* - 1\right)\frac{p_l}{p_h}\left(1 - x_f\right)\right]}{\alpha^*\left(1 - x_f\right) + x_f} \qquad (25)$$

Hence, a feed of x_f concentration cannot be stripped lower than a value of x_{0M} even with an infinitely large membrane area for a **complete mixed** system. To strip beyond this limiting value a cascade-type system or a single unit of plug flow should be used.

5. Cross-flow model for gas separation

A detailed flow diagram is shown in Figure 9. The flow in the high-pressure or reject stream is considered to be of plug flow. On the low-pressure side the permeate stream is pulled into vacuum, so the flow is perpendicular to the membrane. No mixing in both sides is assumed. This cross-flow pattern is an approximation to the actual spiral-wound membrane separator with a high-flux asymmetric membrane resting on a porous support.

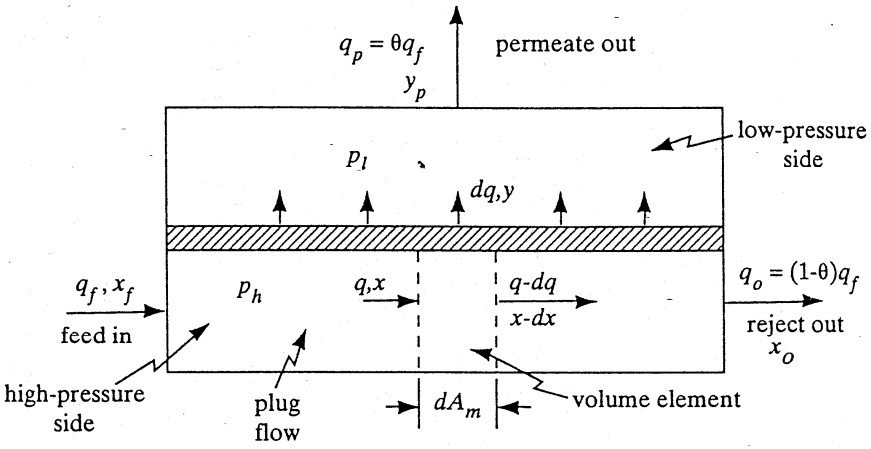


FIGURE 9 *Process flow diagram for cross-flow model.*

The local permeation rate over a differential membrane area dA_m at any point in the stage is

$$ydq = \frac{P_A'}{t}[p_h x - p_l y]dA_m \qquad (26)$$

$$(1-y)dq = \frac{P_B'}{t}[p_h(1-x) - p_l(1-y)]dA_m \qquad (27)$$

where dq is the total flow rate permeating through the area dA_m. Dividing Eq. (26) by (27) gives

$$\frac{y}{1-y} = \frac{\alpha^*[x-(p_l/p_h)y]}{(1-x)-(p_l/p_h)(1-y)} \qquad (28)$$

This relates the permeate composition y to the reject composition x at a point along the path. It is similar to Eq. (16) for complete-mixing.

The solution to the three equations (26) - (28) is

$$\frac{(1-\theta^*)(1-x)}{(1-x_f)} = \left(\frac{u_f - E/D}{u - E/D}\right)^R \left(\frac{u_f - \alpha^* + F}{u - \alpha^* + F}\right)^S \left(\frac{u_f - F}{u - F}\right)^T \qquad (29)$$

where

$$\theta^* = 1 - \frac{q}{q_f}; \qquad i = \frac{x}{1-x}$$

$$u = -Di + \left(D^2 i^2 + 2Ei + F^2\right)^{0.5}$$

$$D = 0.5\left[\frac{(1-\alpha^*)P_l}{P_h} + \alpha^*\right]$$

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

$$F = -0.5\left[\frac{(1-\alpha^*)P_l}{P_h} - 1\right]$$

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

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

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

The term u_f is the value of u at $i = i_f = x_f/(1-x_f)$. The value of θ^* is the fraction permeated up to the value of x in Fig. 9. At the outlet where $x = x_0$, $\theta^* = \theta$, the total fraction permeated.

The total membrane area required is

$$A_m = \frac{tq_f}{P_h P'_B}\int_{i_0}^{i_f} \frac{(1-\theta^*)(1-x)di}{(f_i - i)\left[\frac{1}{1+i} - \frac{P_l}{P_h}\left(\frac{1}{1+f_i}\right)\right]} \qquad (30)$$

where

$$f_i = (Di - F) + \left(D^2 i^2 + 2Ei + F^2\right)^{0.5}$$

values of θ^* in the integral can be obtained from Eq. (29).

Case 1. The values of x_f, x_0, α^*, and P_l/P_h are given and y_p, θ, and A_m, are to be determined. θ^* or θ can be calculated from directly from Eq. (29). Since all other variables are known, y_p can be calculated from Eq. (19). The membrane area A_m is calculated from Eq. (30) numerically.

Case 2. x_f, θ, α^*, and P_l/P_h are given and y_p, x_0, and A_m, are to be determined. This is trial and error. An initial value of x_0 is assumed and substituted into Eq. (19) to calculate y_p.

EXAMPLE 13.6-1. Design of a Membrane Unit Using Cross-Flow

The same conditions for the separation of an air stream as given in Example 13.4-2 for complete mixing are to be used in this example. The process flow streams will be in cross-flow. The given values are $x_f = 0.209$, $\theta = 0.20$, $\alpha^* = 10$, $p_h = 190$ cm Hg, $p_l = 19$ cm Hg, $q_f = 1 \times 10^6$ cm^3(STP)/s, $P'_A = 500 \times 10^{-10}$ cm^3(STP) · cm/(s · cm^2 · cm Hg), and $t = 2.54 \times 10^{-3}$ cm. Do as follows:

(a) Calculate y_p, x_o, and A_m.

(b) Compare the results with Example 13.4-2.

Solution: Since this is the same as Case 2, a value of $x_o = 0.1642$ will be used for the first trial for part (a). Substituting into Eq. (13.6-4)

$$i = i_f = \frac{x_f}{1-x_f} = \frac{0.209}{1-0.209} = 0.2642$$

$$i = \frac{0.1642}{1-0.1642} = 0.1965$$

$$D = 0.5\left[\frac{(1-\alpha^*)p_l}{p_h} + \alpha^*\right]$$

$$= 0.5\left[\frac{(1-10)19}{190} + 10\right] = 4.550$$

$$F = -0.5\left[\frac{(1-\alpha^*)p_l}{p_h} - 1\right]$$

$$= -0.5\left[\frac{(1-10)19}{190} - 1\right] = 0.950$$

$$E = \frac{\alpha^*}{2} - DF = \frac{10}{2} - 4.550(0.950) = 0.6775$$

$$R = \frac{1}{2D-1} = \frac{1}{2(4.550)-1} = 0.12346$$

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

$$= \frac{10(4.550-1)+0.950}{(2\times 4.550-1)(10/2-0.950)} = 1.1111$$

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

$$= \frac{1}{1-4.550-0.6775/0.950} = -0.2346$$

$$u_f = -Di + (D^2i^2 + 2Ei + F^2)^{0.5}$$

$$= -(4.550)(0.2642) + [(4.550)^2(0.2642)^2$$

$$+ 2(0.6775)(0.2642) + (0.950)^2]^{0.5}$$

$$= 0.4427$$

$$u = -(4.550)(0.1965) + [(4.550)^2(0.1965)^2$$

$$+ 2(0.6775)(0.1965) + (0.950)^2]^{0.5}$$

$$= 0.5089$$

$$\frac{(1-\theta^*)(1-x)}{(1-x_f)} = \frac{(1-\theta^*)(1-0.1642)}{(1-0.209)}$$

$$= \left(\frac{0.4427 - 0.6775/4.550}{0.5089 - 0.6775/4.550}\right)^{0.12346}$$

$$\left(\frac{0.4427 - 10 + 0.950}{0.5089 - 10 + 0.950}\right)^{1.1111}$$

$$\left(\frac{0.4427 - 0.950}{0.5089 - 0.950}\right)^{-0.2346}$$

Solving $\theta^* = 0.0992$. This value of 0.0992 does not check the given value of $\theta = 0.200$. However, these values can be used later to solve Eq. (13.6-5).

For the second iteration, a value of $x_o = 0.142$ is assumed and it is used again to solve for θ^* in Eq. (13.6-4), which results in $\theta^* = 0.1482$. For the final iteration, $x_o = 0.1190$ and $\theta^* = \theta = 0.2000$. Several more values are calculated for later use and are for $x_o = 0.187$, $\theta^* = 0.04876$, and for $x_o = 0.209$, $\theta^* = 0$. These values are tabulated in Table 13.6-1.

TABLE 13.6-1. *Calculated Values for Example 13.6-1*

θ^*	x	y_p	F_i
0	0.209	0.6550	0.6404
0.04876	0.1870	0.6383	0.7192
0.0992	0.1642	0.6158	0.8246
0.1482	0.1420	0.5940	0.9603
0.2000	0.1190	0.5690	1.1520

Using the material-balance equation (13.4-8) to calculate y_p,

$$y_p = \frac{x_f - x_o(1-\theta)}{\theta} = \frac{0.209 - 0.1190(1-0.2000)}{0.2000} = 0.5690$$

To calculate y_p at $\theta^* = 0$, Eq. (28) must be used and give $y_p = 0.6550$.

To solve for the area, Eq. (13.6-5) can be written as

$$A_m = \frac{tq_f}{p_h P'_B}\int_{i_o}^{i_f}\left[\frac{(1-\theta^*)(1-x)}{(f_i-i)\left[\frac{1}{1+i}-\frac{p_l}{p_h}\left(\frac{1}{1+f_i}\right)\right]}\right]di = \frac{tq_f}{p_h P'_B}\int_{i_o}^{i_f} F_i\, di \qquad \textbf{(13.6-6)}$$

where the function F_i is defined as above. Values of F_i will be calculated for different values of i in order to integrate the equation. For $\theta^* = 0.200$, $x_o = 0.119$ and from Eq. (13.6-4),

$$i = i_o = \frac{x}{(1-x)} = \frac{0.119}{(1-0.119)} = 0.1351$$

From Eq. (13.6-5),

$$f_i = (Di - F) + (D^2 i^2 + 2Ei + F^2)^{0.5}$$

$$= (4.55 \times 0.1351 - 0.950) + [(4.55)^2(0.1351)^2 + 2(0.6775)(0.1351) + (0.95)^2]^{0.5}$$

$$= 0.8744$$

Using the definition of F_i from Eq. (13.6-6),

$$F_i = \frac{(1-\theta^*)(1-x)}{(f_i-i)\left[\frac{1}{1+i}-\frac{p_l}{p_h}\left(\frac{1}{1+f_i}\right)\right]}$$

$$= \frac{(1-0.200)(1-0.119)}{(0.8744-0.1351)\left[\frac{1}{1+0.1351}-\frac{19}{190}\left(\frac{1}{1+0.8744}\right)\right]}$$

$$= 1.1520$$

Other values of F_i are calculated for the remaining values of θ^* and are tabulated in Table 13.6-1. The integral of Eq. (13.6-6) is obtained by using the values from Table 13.6-1 and plotting F_i versus i to give an area of 0.1082. Finally, substituting into Eq. (13.6-6)

$$A_m = \frac{tq_f}{p_h P'_B}\int_{i_o}^{i_f} F_i\, di = \frac{2.54 \times 10^{-3}(1 \times 10^6)}{190(50 \times 10^{-10})/10}(0.1082)$$

For part (b), from Example 13.4-2, $y_p = 0.5067$ and $A_m = 3.228 \times 10^8$ cm^2. Hence, the cross-flow model yields a higher y_p of 0.5690 compared to 0.5067 for the complete-mixing model. Also, the area for the cross-flow model is 10% less than for the complete-mixing model.

6. Countercurrent-flow model for gas separation

A detailed flow diagram is shown in Figure 10. Making a total and a component balance for A over the volume element and the reject,

$$q = q_0 + q' \qquad (31)$$

$$qx = q_0 x_0 + q' y \qquad (32)$$

Differentiating Eq. (32)

$$d(qx) = 0 + d(q' y) \qquad (33)$$

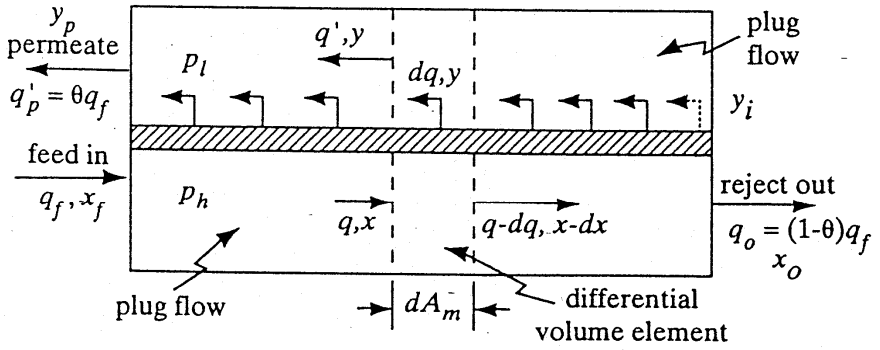


FIGURE 10 *Flow diagram for the countercurrent-flow model.*

A balance for component A on the high- and low-pressure sides of the volume element gives

$$qx = (q - dq)(x - dx) + ydq \tag{34}$$

Simplifying to become

$$ydq = qdx + xdq = d(qx) \tag{35}$$

The local flux out of the element with area dA_m is

$$ydq = \frac{P_A'}{t}(p_h x - p_l y)dA_m \tag{36}$$

Combining Eqs. (33), (35), and (36)

$$d(q'y) = d(qx) = ydq = \frac{P_A'}{t}(p_h x - p_l y)dA_m \tag{37}$$

Similarly, for component B,

$$d[q'(1-y)] = d[q(1-x)] = \frac{P_B'}{t}[p_h(1-x) - p_l(1-y)]dA_m \tag{38}$$

Combining Eqs. (31) and (32) to eliminate q' and multiplying dx,

$$q_0 dx = \left(\frac{x-y}{y-x_0}\right)(-qdx) \tag{39}$$

$$\text{Since } d[xq(1-x)] = xd[q(1-x)] + q(1-x)dx \tag{40}$$
$$= (1-x)d(qx) + qxd(1-x)$$

we have

$$qdx = (1-x)d(qx) - xd[q(1-x)] \tag{41}$$

Substituting qdx from (41), d(qx) from (37), and d[q(1-x)] from (38) into Eq. (39) gives

$$\left(\frac{q_0 t}{p_l P_B'}\right)\frac{dx}{dA_m} = \left(\frac{y-x}{y-x_0}\right)\left\{(1-x)\alpha^*(rx-y) - x[r(1-x)-(1-y)]\right\} \tag{42}$$

where $r = p_h / p_l$ and $\alpha^* = P_A'/\ P_B'$.

Similarly, we can obtain

$$q_0 dy = \left(\frac{x-y}{x-x_0}\right)(-q'\,dy) \tag{43}$$

$$\left(\frac{q_0 t}{p_l P_B}\right)\frac{dy}{dA_m} = \left(\frac{x-y}{x-x_0}\right)\left\{(1-y)\alpha^*(rx-y) - y[r(1-x)-(1-y)]\right\} \tag{44}$$

At the outlet of the residue stream of composition x_0, the permeate $y = y_i$, and x_0 are related by Eq. (16), which is given below as Eq. (45)

$$\frac{y_i}{1-y_i} = \frac{\alpha^*[x_0 - (p_l/p_h)y_i]}{(1-x_0) - (p_l/p_h)(1-y_i)} \tag{45}$$

Eqs. (42) and (44) are solved simultaneously by numerical methods starting at the high-pressure outlet stream of composition x_0. The area A_m can be arbitrarily set equal to zero at this outlet and a negative area will be obtained whose sign must be reversed.

7. Effects of processing variables on gas separation by membranes

7.1 Effects of pressure ratio and separation factor on recovery

By using the complete-mixing model (Eq. 16), the effects of pressure ratio, p_h/p_l, and separation factor, α^*, on permeate purity are plotted in Figure 11 for a fixed feed composition (30%). Above an α^* of 20 or a pressure ratio of 6, the product purity is not greatly affected.

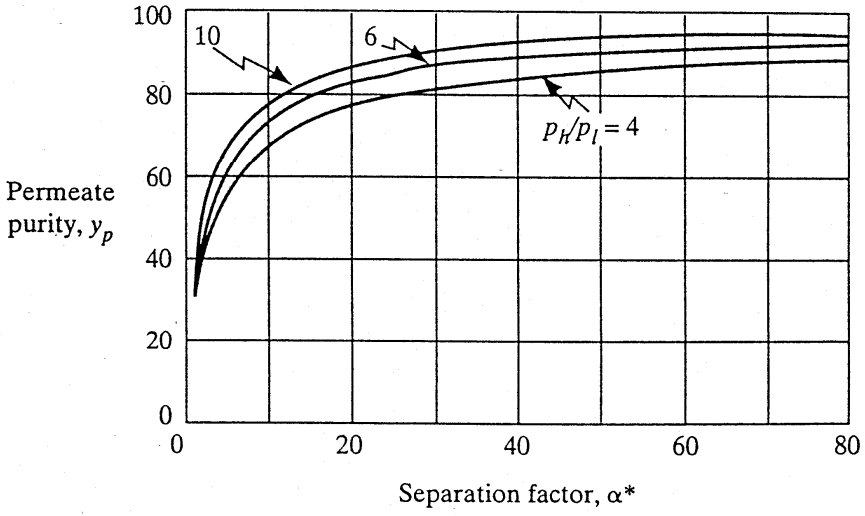


FIGURE 11 *Effects of separation factor and pressure ratio on permeate purity. (Feed x_f = 0.30.)* [From "Membranes Separate Gases Selectively," by D. J. Stookey, C. J. Patton, and G. L. Malcolm, *Chem. Eng. Progr.*, **82**(11), 36 (1986). Reproduced by permission of the American Institute of Chemical Engineers, 1986.]

7.2 Effects of process flow patterns on separation and area

Figure 12 shows the permeate concentration versus stage cut, θ, for a feed of air (x_0 = 0.209 for oxygen) with α^* = 10 and p_h/p_l = 5. As expected, the countercurrent flow pattern gives the best separation, followed by cross-flow, cocurrent, and the complete-mixing pattern offers the lowest separation. All four patterns become identical at a θ value of 0 or 1.

The required membrane areas to achieve the same separation for all four types of flow are within about 10% of each other. The countercurrent flow again gives the lowest area required.

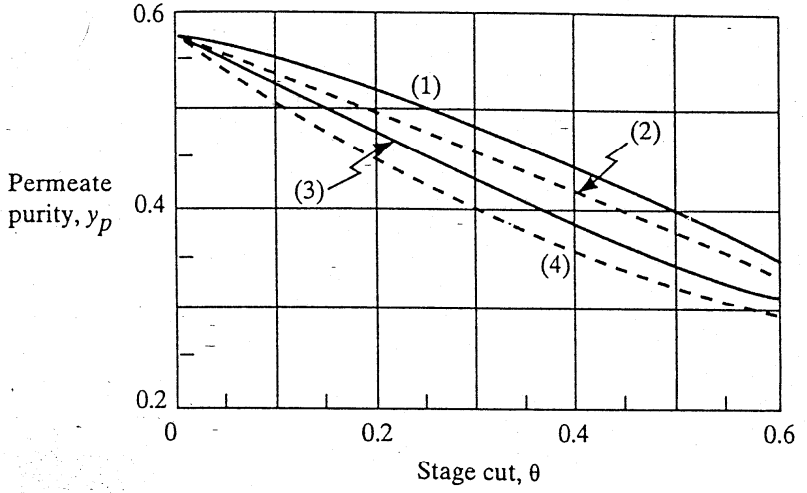


FIGURE 12 *Effect of stage cut and flow pattern on permeate purity. Operating conditions for air are as follows: x_f = 0.209, α^* = 10, p_h/p_l = 380 cm Hg/76 cm Hg = 5. P'_A = 500 × 10^{-10} $cm^3(STP) \cdot cm/s \cdot cm^2 \cdot cm$ Hg. (1) countercurrent flow, (2) cross-flow, (3) cocurrent flow, (4) complete mixing*

Reverse osmosis

In osmosis, solvent transports from a dilute solute or salt solution to a concentrated solute or salt solution across a semipermeable membrane which allows passage of the solvent but impedes passage of the salt solutes. In figure 1a the solvent water normally flows through the membrane to the salt solution. The levels of both liquids are the same. The solvent flow can be reduced by exerting a pressure on the salt-solution side and membrane, as shown in Figure 1b, until at a certain pressure, called the ***osmotic pressure*** π of the salt solution, equilibrium is reached and the amount of solvent passing in opposite directions is equal.

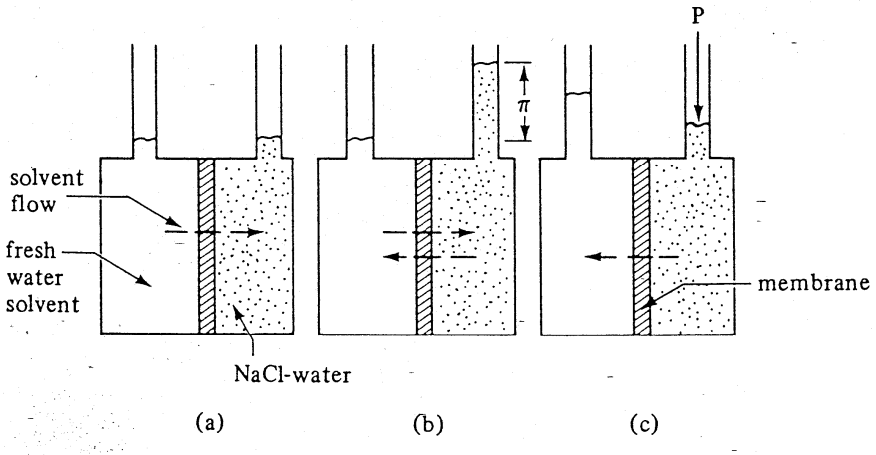


FIGURE 1 *Osmosis and reverse osmosis: (a) osmosis, (b) osmotic equilibrium, (c) reverse osmosis.*

The chemical potentials of the solvent on both sides of the membrane are equal. The osmotic pressure depends on the property of the solution, but not the membrane provided it is truly semipermeable. To reverse the flow of water so that it flows from the salt solution to the fresh solvent as in Figure 1c, the pressure is increased above the osmotic pressure on the solution side.

This phenomenon, called *reverse osmosis*, is used in many processes, such as the desalination of seawater to produce fresh water. Reverse osmosis can operate at ambient temperature without phase change. It is useful for separating thermally and chemically unstable products.

1. Osmotic pressure of solutions

The osmotic pressure of a solution is proportional to the concentration of the solute and temperature T. The relationship is similar to that for pressure of an ideal gas. For example, for dilute water solutions,

$$\pi = \frac{n}{V_m} RT \qquad (1)$$

where n is the number of kg mol of solute, V_m the volume of pure solvent water in m^3 associated with *n* kg mol of solute., R is the gas constant, and T is temperature in K. If a solute exists as two or more ions in solution, *n* represents the total number of ions. For more concentrated solutions, Eq. (1) is modified using an osmotic coefficient ϕ, which is the ratio of the actual osmotic pressure π to the ideal π calculated from the equation. Some experimental values of π are listed in Table 1 for NaCl, sucrose, and seawater solutions.

TABLE 1 *Osmotic Pressure of Various Aqueous Solutions at 25°C (P1, S3, S5)*

Sodium Chloride Solutions			*Sea Salt Solutions*		*Sucrose Solutions*	
g mol NaCl / kg H_2O	*Density (kg/m^3)*	*Osmotic Pressure (atm)*	*Wt. % Salts*	*Osmotic Pressure (atm)*	*Solute Mol. Frac. × 10^3*	*Osmotic Pressure (atm)*
0	997.0	0	0	0	0	0
0.01	997.4	0.47	1.00	7.10	1.798	2.48
0.10	1001.1	4.56	3.45*	25.02	5.375	7.48
0.50	1017.2	22.55	7.50	58.43	10.69	15.31
1.00	1036.2	45.80	10.00	82.12	17.70	26.33
2.00	1072.3	96.2				

* Value for standard seawater.

2. Types of membranes for reverse osmosis

The cellulose acetate membrane is the most important one used in reverse osmosis. The asymmetric membrane is made as a composite film in which a thin dense layer about 0.1 to 10 μm thick of extremely fine pores supported upon a much thicker (50 to 125 μm) layer of microporous sponge with little resistance to permeation. The thin, dense layer has the ability to block the passage of quite small solute molecules. In desalination the membrane rejects the salt solute and allows the solvent water to pass through.

Another important membrane useful for seawater, wastewater, nickel-plating rinse solutions is the synthetic aromatic polyamide membrane “Permasep” made in the form of very fine hollow fibres.

3. Flux equations for reverse osmosis

There are two basic types of mass-transport mechanisms in membranes. In the first type, using tight membranes, which are capable of retaining solutes of about 10 $\overset{o}{A}$ in size or less, diffusion-type transport mainly occurs. Both the solute and the solvent migrate by molecular or Fickian diffusion in the polymer, driven by the concentration gradients set up in the membrane by the applied pressure difference. In the second type, a sieve-type mechanism occurs where the solvent moves through the micropores in viscous flow, and the solute molecules small enough to pass through the pores are carried out by convection with the solvent.

For diffusion-type membranes, the steady-state equations governing the transport of solvent and solute are given below:

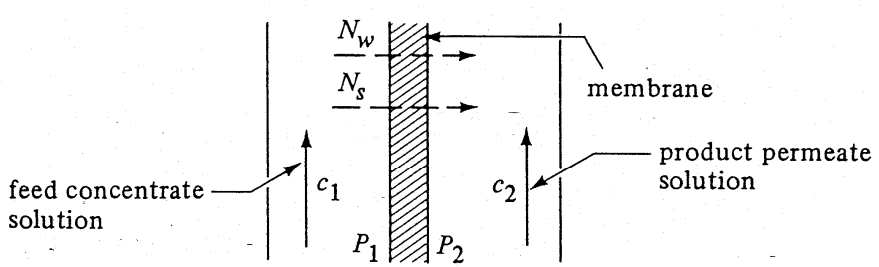


FIGURE 2 *Concentrations and fluxes in reverse-osmosis process.*

$$N_w = \frac{P_w}{L_m}(\Delta P - \Delta\pi) = A_w(\Delta P - \Delta\pi) \quad (2)$$

$$P_w = \frac{D_w \bar{c}_w V_w}{RT} \quad (3)$$

$$A_w = \frac{P_w}{L_m} \quad (4)$$

$$N_s = \frac{D_s K_s}{L_m}(c_1 - c_2) = A_s(c_1 - c_2) \quad (5)$$

$$A_s = \frac{D_s K_s}{L_m} \quad (6)$$

where N_w and N_s are the solvent and solute fluxes in kg/s m^2; P_w the solvent membrane permeability, kg/s m atm; L_m the membrane thickness in m; A_w and A_s the solvent and solute permeability constants, kg/s m^2 atm; $\Delta P = P_1 - P_2$ (hydrostatic pressure difference with P_1 as the pressure exerted on feed and P_2 on product solution), atm; $\Delta\pi = \pi_1 - \pi_2$ (osmotic pressure of feed solution - osmotic pressure of product solution), atm; D_w and D_s are the diffusivity of solvent and solute in membrane, m^2/s; $\bar{c}_w$ the mean concentration of solvent in membrane, kg solvent/m^3; V_w the molar volume of solvent, m^3/kg mol solvent; R the gas constant, 82.057×10^{-3} m^3 atm/kg mol K; and T the temperature, K. Note that the subscript 1 is the feed or upstream side of the membrane and 2 the product or downstream side of the membrane; $K_s = c_m / c$ (distribution coefficient).

At steady state, the solute diffusing through the membrane must equal the amount of solute leaving in the downstream or product (permeate) solution,

$$N_s = \frac{N_w c_2}{c_{w2}} \qquad (7)$$

where c_{w2} is the concentration of solvent in stream 2, kg solvent/m^3. If the stream 2 is dilute in solute, c_{w2} is approximately the density of the solvent. In reverse osmosis, the solute rejection R is defined as the concentration difference across the membrane divided by the bulk concentration on the feed or concentrate side (fraction of solute remaining in the feed stream):

$$R = \frac{c_1 - c_2}{c_1} = 1 - \frac{c_2}{c_1} \qquad (8)$$

c_2/c_1 can be obtained by substituting Eqs. (2) and (5) to (7).

We have the total flux = $\frac{N_s}{c_2} = \frac{N_w}{c_{w2}}$

$$\frac{A_s(c_1 - c_2)}{c_2} = \frac{A_w(\Delta P - \Delta\pi)}{c_{w2}}$$

$$\frac{c_1 - c_2}{c_2} = \frac{c_1}{c_2} - 1 = \frac{A_w(\Delta P - \Delta\pi)}{A_s c_{w2}}$$

If we define $B = \frac{A_w}{A_s c_{w2}}$ (9)

then

$$\frac{c_1 - c_2}{c_2} = B(\Delta P - \Delta\pi)$$

$$\frac{c_1}{c_2} = B(\Delta P - \Delta\pi) + 1$$

$$R = \frac{c_1 - c_2}{c_1} = \frac{c_1 - c_2}{c_2}\left(\frac{c_2}{c_1}\right) = \frac{B(\Delta P - \Delta\pi)}{1 + B(\Delta P - \Delta\pi)} \qquad (10)$$

where B is in 1/atm, which must be determined experimentally. Usually, (P_w / L_m) or A_w and $(D_s K_s / L_m)$ or A_s are given in the literature.

Example 1.Determination of membrane permeability
Experiments at 25 ^{o}C were performed to determine the permeabilities of a cellulose acetate membrane. The laboratory test section shown in Figure 3 has a membrane area A = 2×10^{-3} m^2. The inlet feed solution concentration of NaCl is c_1 = 10 g NaCl/L solution (ρ_1 = 1004 kg solution/m^3). The water recovery is assumed low so that the concentration c_1 in the entering feed solution flowing past the membrane and the concentration of the reject solution are equal. The product solution contains c_2 = 0.39 g NaCl/L solution (ρ_2 = 997 kg solution/m^3) and its flow rate is 1.92×10^{-8} m^3 solution/s. A pressure differential of 5514 kPa (54.42 atm) is used. Calculate the permeability constants and the solute rejection R.

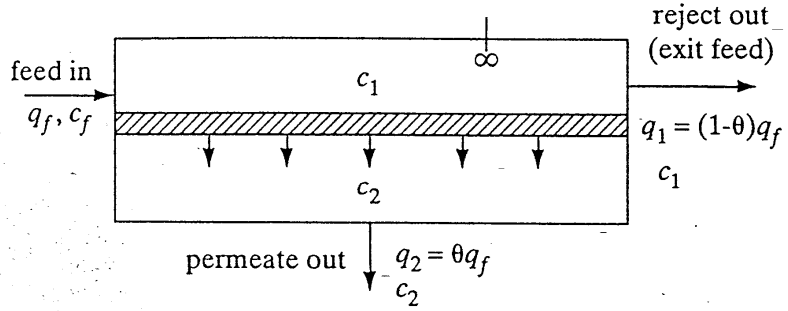


FIGURE 3 *Process flow for complete-mixing model for reverse osmosis.*

Solution. Since c_2 is very low. c_{w2} can be assumed to as the density of water. c_{w2} = 997 kg solution/m^3.

The water flux is

$$N_w = \frac{F\rho_2}{A} = \frac{\left(1.92\times10^{-8}\ m^3/s\right)\left(997\ kg\ solvent/m^3\right)}{2.0\times10^{-3}\ m^2}$$

$$= 9.57\times10^{-3}\ kg\ solvent/\left(s\ m^2\right)$$

$$N_s = \frac{N_w c_2}{c_{w2}} = \frac{9.57\times10^{-3}\times0.39}{997}$$

$$= 3.744\times10^{-6}\ kg\ solute\ NaCl/\left(s\ m^2\right)$$

The osmotic pressure is found from Table 1,

π_1 = 7.80 atm, π_2 = 0.32 atm

$\Delta\pi = \pi_1 - \pi_2 = 7.80 - 0.32 = 7.48$ atm

ΔP = 54.42 atm (given)

$$N_w = 9.57\times10^{-3}\ kg\ solvent/\left(s\ m^2\right)$$

$$= \frac{P_w}{L_m}\left(\Delta P - \Delta\pi\right) = \frac{P_w}{L_m}\left(54.42 - 7.48\right)$$

Hence,

$$\frac{P_w}{L_m} = A_w = 2.039\times10^{-4}\ kg\ solvent/\left(s\ m^2\ atm\right)$$

$$N_s = 3.744\times10^{-6}\ kg\ solute\ NaCl/\left(s\ m^2\right)$$

$$= \frac{D_s K_s}{L_m}\left(c_1 - c_2\right) = \frac{D_s K_s}{L_m}\left(10 - 0.39\right)$$

$$\frac{D_s K_s}{L_m} = A_s = 3.896\times10^{-7}\ m/s$$

$$R = \left(c_1 - c_2\right)/c_1 = (10 - 0.39)/10 = 0.961$$

4. Effects of operating variables

The operating pressures used in commercial reverse osmosis units range from 10 to 100 atm. The solvent flux depends only on the net pressure difference, while the solute flux depends only on the concentration difference. Hence, as the feed pressure is increased, solvent or water flow through the membrane increases and the solute flow remains approximately constant, giving a lower solute concentration in the product solution.

Example 2. Prediction of performance in a RO unit

A reverse-osmosis membrane to be used at 25 °C for a NaCl feed solution containing 2.5 g NaCl/L (ρ = 999 kg/m^3) has a water permeability constant A_w = 4.81×10^{-4} kg/s m^2 atm and a solute (NaCl) permeability constant $A_s = 4.42\times10^{-7}$ m/s. Calculate the water flux and solute flux through the membrane using a ΔP = 27.20 atm, and the solute rejection R. Also calculate c_2 of the product solution.

Solution. In the feed solution, c_1 = 2.5 kg NaCl/ m^3, and ρ_1 = 999 kg solution/m^3. Hence, for the feed, 999 – 2.5 = 996.5 kg H_2O in 1.0 m^3 solution; also for the feed, (2.50 × 1000)/(996.5 × 58.45) = 0.04292 g mol NaCl/kg H_2O so the osmotic pressure π_1 = 1,97 atm. Since the product solution c_2 is unknown, a

value of c_2 = 0.1 kg NaCl/ m^3 will be assumed. Because the product is dilute, ρ_2 = 997 kg solution/m^3 and C_{w2} = 997 kg solvent/m^3. Then for the product solution, (0.1 × 1000)/(996.5 × 58.45) = 0.00172 g mol NaCl/kg H_2O and the osmotic pressure π_2 = 0.08 atm.

$$\Delta\pi = \pi_1 - \pi_2 = 1.97 - 0.08 = 1.89 \text{ atm}$$

$$N_w = A_w(\Delta P - \Delta\pi) = 4.81\times10^{-4}(27.20 - 1.89)$$

$$= 1.217\times10^{-2} \text{ kg } H_2O/\text{s m}^2$$

$$B = \frac{A_w}{A_s C_{w2}} = \frac{4.81\times10^{-4}}{4.42\times10^{-7}\times997} = 1.092 \text{ atm}^{-1}$$

$$R = \frac{B(\Delta P - \Delta\pi)}{1 + B(\Delta P - \Delta\pi)} = \frac{1.092(27.20 - 1.89)}{1 + 1.092(27.20 - 1.89)} = 0.965$$

Using this value of R to re-calculate c_2.

$$R = 0.965 = \frac{c_1 - c_2}{c_1} = \frac{2.50 - c_2}{2.50}$$

Solving, c_2 = 0.0875 kg NaCl/ m^3 for the product solution. This is close enough to the assumed value of c_2 = 0.10 so that π_2 will not change significantly on the second trial. Hence, the final value of c_2 is 0.0875 kg NaCl/ m^3.

$$N_s = A_s(c_1 - c_2) = 4.42\times10^{-7}(2.50 - 0.0875)$$

$$= 1.066\times10^{-6} \text{ kg NaCl/s m}^2$$

5. Concentration polarization in reverse osmosis diffusion model

The nearly complete rejection of solute by the membrane leads to a higher concentration at the membrane surface than in the bulk solution, this effect is called concentration polarization. Concentration polarization reduces the flux of solvent (water) because the increase in osmotic pressure reduces the driving force for solvent transport. Also the solute flux increases since the solute concentration increases at the boundary. Hence, often the ΔP must be increased to compensate the concentration polarization, this gives higher power costs.

The concentration polarization ratio, β, is defined as the ratio of the salt concentration at the membrane surface (c_{1s}) to the salt concentration in the bulk feed stream c_1. At steady state, the solute carried to the membrane by the water flux almost equals the amount of solute diffusing back to the solution and the flux through the membrane.

$$N_w c_1 = k_c(c_{1s} - c_1) + N_w c_2 \qquad (11)$$

$$\beta = \frac{c_{1s}}{c_1} = \frac{c_{1s} - c_1 + c_1}{c_1} = \frac{c_{1s} - c_1}{c_1} + 1 = \frac{N_w R}{k_c} + 1 \qquad (12)$$

where k_c is the mass transfer coefficient of solute in the boundary layer, N_w is in m/s or cm/s.

By assuming that the osmotic pressure is directly proportional to the concentration, which is approximately correct, the osmotic pressure difference may be modified as

$$\Delta\pi = \beta\pi_1 - \pi_2 \qquad (13)$$

The diffusion flux of the solute is

$$N_s = A_s(\beta c_1 - c_2) \qquad (14)$$

The usual concentration polarization ratio is 1.2 to 2.0, i.e., the concentration in the boundary layer is 1.2 to 2.0 times c_1 in the bulk feed solution. This ratio is often difficult to predict. A polarization ratio of less than 1.1 can be neglected. A large value of β indicates that the performance should be improved by changing the dimensions or velocities in the separator to give better mass transfer.

Example 3.

A hollow-fiber permeator with outside diameter d_o = 300 μm and inside diameter d_i = 200 μm gives a water flux of 10 gal/day-ft^2 with 0.1 M NaCl solution at 20 ^{o}C, and the salt rejection is 97%. Feed solution flows normal to the fibers at an average superficial velocity of 0.5 cm/s. Is concentration polarization significant?

Solution:

For 10 gal/day-ft^2,

$$N_w = 10 \times \frac{3785}{24 \times 3600 \times 929} = 4.72 \times 10^{-4} \text{ cm/s}$$

$$Re = \frac{d_o u \rho}{\mu} = \frac{0.03 \text{ cm} \times 0.5 \text{ cm/s} \times 1 \text{ g/cm}^3}{0.01 \text{ g/cm-s}} = 1.5$$

The diffusivity of NaCl is $D_s = 1.6 \times 10^{-5}$ cm^2/s

$$Sc = \frac{\mu}{\rho D_s} = \frac{0.01}{1 \times 1.6 \times 10^{-5}} = 625$$

For flow normal to cylinders and $1 < Re < 10^4$, the following correlation can be used:

$$Sh / Sc^{0.3} = 0.35 + 0.56\,Re^{0.52}$$

so

$$Sh = \left[0.35 + 0.56(1.5)^{0.52}\right] 625^{0.3} = 7.18$$

and

$$k_c = \frac{Sh(D_s)}{d_o} = \frac{7.18\left(1.6 \times 10^{-5}\right)}{0.03} = 3.83 \times 10^{-3} \text{ cm/s}$$

Hence, the concentration polarization ratio is

$$\beta = \frac{N_w R}{k_c} + 1 = \frac{4.72 \times 10^{-4}(0.97)}{3.83 \times 10^{-3}} + 1 = 1.12$$

which is close to unity, so the concentration polarization is not significant.

6. Frictional pressure drop

The equipment used for reverse osmosis is similar to that for gas permeation membrane processes. For hollow-fiber membranes, which have a bundle with thousands of closely packed fibers and are sealed in a metal cylinder, the feed solution passes radially across the fibers or flows parallel to the fibers on the shell side, and the product water is collected from the fiber lumens at one end of the bundle. For high production rates, feed water is passed in parallel through many permeators, and the residue streams may be combined and passed through another set of permeators, as shown in Figure 4.

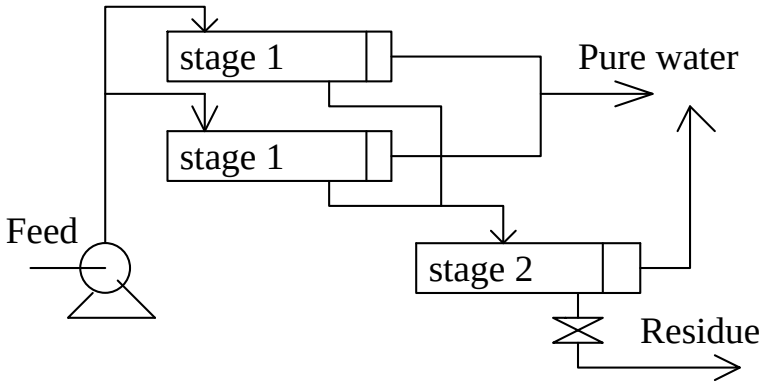


Figure 4. Two stage reverse-osmosis system

With this arrangement, the velocity on the shell side is kept high to get good flow distribution and minimize concentration polarization.

The flow inside the fibers is laminar, the pressure gradient caused by skin friction is given by the derivative form of the Hagen-Poiseuille equation:

$$\frac{dp_s}{dL} = \frac{32\bar{V}\mu}{g_c D^2} \tag{15}$$

where $\bar{V}$ is the average velocity, μ is the viscosity, g_c is the Newton's-law proportionality factor, and D is the tube diameter. The velocity increases with distance from the closed end of the fiber, and the incremental change in flow rate is the flux per unit wall area times the incremental area:

$$\frac{\pi D^2}{4} d\bar{V} = N_w \pi D dL \tag{16}$$

$$\frac{d\bar{V}}{dL} = \frac{4N_w}{D} \tag{17}$$

Usually the water flux N_w changes along the length of the separator, since increasing salt concentration increases $\Delta\pi$, and the pressure build up inside the fibers decreases ΔP. To simplify the analysis and to get an approximate solution, N_w is assumed constant, integrating Eq. (17) gives

$$\bar{V} = \frac{4N_w L}{D} \tag{18}$$

Substituting Eq. (18) into Eq. (15) and integrating,

$$\frac{dp_s}{dL} = \frac{128N_w\mu L}{g_c D^3} \tag{19}$$

$$\Delta p_s = \frac{128N_w\mu}{g_c D^3}\frac{L^2}{2} \tag{20}$$

Example 4.

(a) For the permeator of Example 3, estimate the exit velocity and the pressure drop within the fibers if the fiber length is 3 m and the average water flux is 10 gal/day-ft^2 based on the external area.

(b) What is the pressure drop if the fibers are open at both ends?

Solution:

(a) Covert the flux to N_w based on the internal area:

$$N_w = 4.72\times10^{-4}\frac{d_o}{d_i} = 4.72\times10^{-4}\frac{300}{200} = 7.08\times10^{-4}\ \text{cm/s}$$

$$= 7.08\times10^{-6}\ \text{m/s}$$

μ=1 cP = 10^{-3} Pa-s, D = d_i = 200x10^{-6} m

$$\bar{V} = \frac{4N_w L}{D} = \frac{4\left(7.08\times10^{-6}\right)(3)}{200\times10^{-6}} = 0.425\ \text{m/s}$$

$$\Delta p_s = \frac{128N_w\mu}{g_c D^3}\frac{L^2}{2} = \frac{128\left(7.08\times10^{-6}\right)\left(10^{-3}\right)}{\left(2\times10^{-4}\right)^3}\frac{3^2}{2}$$

$$= 5.1\times10^5\ \text{Pa} = 5.03\ \text{atm}$$

This is a significant pressure drop, but if the feed is 50 atm and $\Delta\pi$ goes from 5 atm in the feed to 10 atm at the discharge, the driving force for water transport ($\Delta P - \Delta\pi$) has a maximum value of 50 - 5 = 45 and a minimum of 45 - 10 = 35, so the assumption of constant flux is not greatly in error.

(b) If the fibers are open at both ends, the effective length is 1.5 m and the exit velocity is half of (a). The pressure drop 1/4 as large as it was:

$$\Delta P = \frac{5.03}{4} = 1.26 \text{ atm}$$

The pressure drop in flat-sheet membranes for reverse osmosis can be ignored since the mass transfer area is lower than that for hollow-fiber.

Ultrafiltration Membrane Processes

Ultrafiltration is similar to reverse osmosis. It is a pressure-driven process where the solvent, and small solute molecules pass through the membrane and are collected as permeate. Large solute molecules cannot pass through the membrane and are recovered in a concentrated solution. The solutes or molecules to be separated generally have molecular weights greater than 500 and up to 1,000,000 or more, such as proteins, polymers, and starches.

Ultrafiltration is also used to separate a mixture of different molecular weight proteins. The molecular weight cut-off of the membrane is defined as the molecular weight of globular proteins, which are 90% retained by the membrane.

The equipment for ultrafiltration is also similar to that used for reverse osmosis and gas separation processes. The rejection, often called retention in ultrafiltration, is defined in the same way as reverse osmosis.

In ultrafiltration, the concentration in moles/liter of the large molecules is usually small, so the osmotic

pressure is very low and is negligible. Hence, the diffusion flux can be simplified as

$$N_w = A_w(\Delta P) \qquad (21)$$

Ultrafiltration units operate at about 5 to 100 psi pressure drop compared with 400 to 2000 for reverse osmosis.

Since the solute is rejected by the membrane, it accumulates and starts to build up at the surface of the membrane. As pressure drop is increased and/or concentration of the solute is increased, concentration polarization occurs, which is much more severe than in reverse osmosis. This is shown in Figure 5a, where c_1 is the solute concentration in the bulk solution, c_s is the solute concentration at the surface of the membrane.

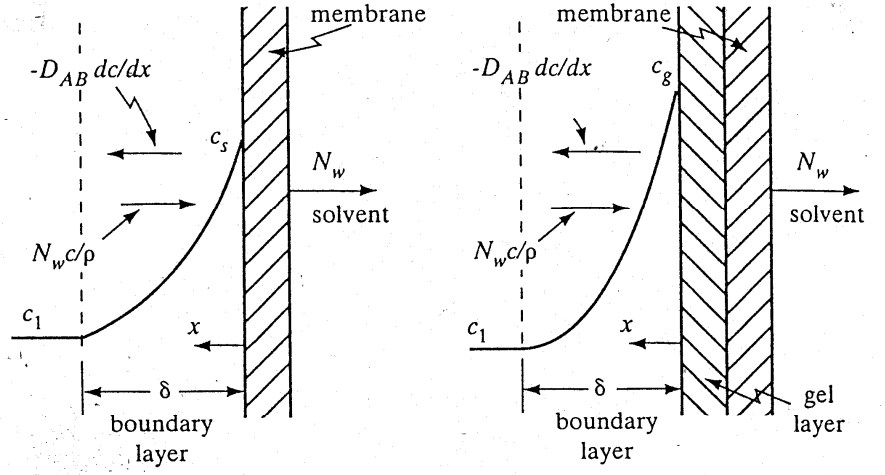


FIGURE 5 *Concentration polarization in ultrafiltration: (a) concentration profile before gel formation, (b) concentration profile with a gel layer formed at membrane surface.*

As the pressure drop increases, this increases the solvent flux N_w to and through the membrane. This gives a higher convective transport of the solute to the membrane. The concentration c_s increases and gives a larger back molecular diffusion of solute from the membrane to the bulk solution. At steady state the convection flux equals the diffusion flux,

$$\frac{N_w c}{\rho} = -D_{AB}\frac{dc}{dx} \qquad (22)$$

where $N_w c/\rho$
$=$[kg solvent/(s m^2)](kg solute/m^3)/(kg solvent/m^3)
$=$ kg solute/(s m^2); D_{AB} is diffusivity of solute in solvent, m^2/s; and x is distance, m. Integrating this equation between the limits of $x = 0$ and $c = c_s$, and $x = \delta$ and $c = c_1$,

$$\frac{N_w}{\rho} = \frac{D_{AB}}{\delta}\ln\left(\frac{c_s}{c_1}\right) = k_c \ln\left(\frac{c_s}{c_1}\right) \qquad (23)$$

where k_c is the mass-transfer coefficient, m/s.

Further increases in pressure drop increase the value of c_s to a limiting concentration where the accumulated solute forms a semisolid gel where $c_s = c_g$, as shown in Figure 5b. Still further increases in pressure drop do not change c_g and the membrane is said to be "gel polarized". Then Eq. (23) becomes

$$\frac{N_w}{\rho} = k_c \ln\left(\frac{c_g}{c_1}\right) \qquad (24)$$

With increases in pressure drop, the gel layer increases in thickness and this causes the solvent flux to decrease because of the added gel layer resistance.

The added gel layer resistance next to the membrane causes an increased resistance to solvent flux is given by

$$N_w = \frac{\Delta P}{1/A_w + R_g}$$

where $1/A_w$ is the membrane resistance and R_g is the variable gel layer resistance, (s m^2 atm)/kg solvent. The solvent flux in this gel-polarized regime is independent of pressure difference and is determined by Eq. (24) for back diffusion.

Effects of processing variables in ultrafiltration

A plot of typical experimental data of flux versus pressure difference is shown in Figure 6. At low pressure differences and/or low solute concentrations the data follow Eq. (21). For a given bulk concentration, c_1, the flux approaches a constant value at high pressure differences. Also, more dilute protein concentrations give higher flux rates as expected from Eq. (24). Most commercial applications are flux limited by concentration polarization and operate in the region where the flux is almost independent of pressure difference.

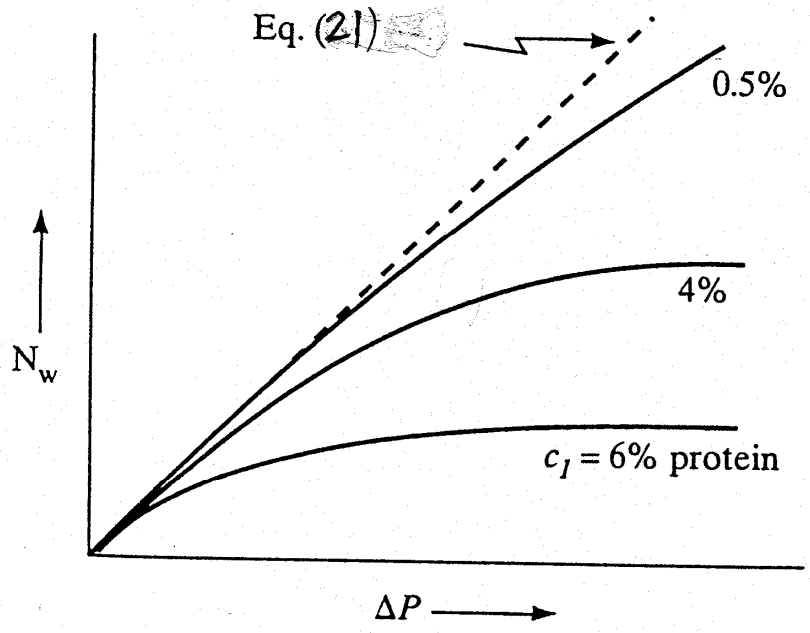


FIGURE 6 *Effect of pressure difference on solvent flux.*

Using experimental data, a plot of N_w/ρ versus $\ln(c_1)$ is a straight line with the negative slope of k_c, the mass-transfer coefficient, as shown by Eq. (24). These plots also give the value of c_g, the gel concentration. Data show that the gel concentration for many macromolecule solutions is about 25 wt%, with a range of 5 to 50%. For colloidal dispersion it is about 65 wt%, with a range of 50 to 75%.

The concentration polarization effects for hollow fibers are often small because of the low solvent flux. Hence Eq. (21) describes the flux. In order to increase the ultrafiltration solvent flux, cross-flow of fluid past the membrane can be used to sweep away part of the polarized layer, thereby increasing k_c. Higher velocities and other methods are used to increase turbulence, and hence, k_c. In most cases the solvent flux is too small to operate in a single-pass mode. It is necessary to recirculate the feed by the membrane with recirculation rates of 10/1 to 100/1 often used.