Chapter 15

Membrane Separation Processes

INTRODUCTION

Membrane processes are state-of-the-art separation technologies that show continued promise for technical growth and wide-scale commercialization. They are used in many industries for process stream and product concentration, purification, and fractionation. The need for membrane research and development (R&D) is important because of the increasing use of membrane technology in traditional and emerging engineering fields. Membrane processes are increasingly finding their way into the growing engineering areas of biotechnology, green engineering, specialty chemical manufacture, biomedical engineering, as well as the traditional chemical process industry. Membrane technology is also being looked at as either a replacement for or supplement to traditional separations such as distillation (Chapter 9) or extraction (Chapter 12). Membrane processes are generally more efficient and effective since they can simultaneously concentrate and purify, and can perform separations at ambient conditions.[1]

Membrane unit operations are often characterized by the following parameters: driving force utilized, membrane type/structure, and species being separated. The following membrane unit operations utilize a pressure driving force to separate a liquid feed into a liquid *permeate* and *retentate*: reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. They are listed in ascending order in their ability to separate a liquid feed based on solute size. *Reverse osmosis* uses non-porous membranes and can separate down to the ionic level as with the example of seawater in the rejection of dissolved salt. *Nanofiltration* performs separations at the nanometer range. *Ultrafiltration* uses porous membranes and separates components of molecular weight ranging from the low thousand to several hundred thousand molecules; an example includes components of biochemical processing. *Microfiltration* uses much more porous membranes and is typically used in the macromolecular range to remove particulate or larger biological matter from a feed stream (e.g., in the range of 0.05–2.5 μm).[1,2]

Mass Transfer Operations for the Practicing Engineer. By Louis Theodore and Francesco Ricci

Dialysis membrane processes use a concentration driving force for separation of liquid feeds across a semipermeable membrane with the major application in the medical field of hemodialysis. *Electrodialysis* separates a liquid feed solution through ion selective membranes by means of an electrical driving force and is widely used in water purification and industrial processing. *Gas separation* processes can be divided into two categories—*gas permeation* through non-porous membranes and *gas diffusion* through porous membranes. Both of these processes utilize a concentration driving force. The gas permeation processes are used extensively in industry to separate air into purified nitrogen and enriched oxygen. Another commercial application is hydrogen recovery in petroleum refineries.[1]

Since membrane separation processes are one of the newer (relatively speaking) technologies being applied in practice, the subject matter is and has been introduced into the engineering curriculum. There are four major membrane processes of interest to the practicing engineer:

1 reverse osmosis (hyperfiltration),

2 ultrafiltration,

3 microfiltration, and

4 gas permeation

The four processes have their differences. The main difference between reverse osmosis (RO) and ultrafiltration (UF) is that the size/diameter of the particles or molecules in solution to be separated is smaller in RO. In microfiltration (MF), the particles to be separated/concentrated are generally solids or colloids rather than molecules in solution. Gas permeation (GP) is another membrane process that employs a nonporous semipermeable membrane to "fractionate" a gaseous stream.

The heart of the membrane process is the membrane itself. A membrane is an ultra-thin semipermeable barrier separating two fluids that permits the transport of certain species through the barrier from one fluid to the other. The membrane is typically made from various polymers such as cellulose acetate or polysulfone, but ceramic and metallic membranes are also used in some applications. The membrane is selective since it permits the transport of certain species while rejecting others. The term semipermeable is frequently used to describe this selective action.[1]

The presentation to follow will key on the above four membrane separation processes, particularly RO because of its widespread use in desalinization applications. RO is reviewed first and receives the bulk of the treatment. This is then followed by UF, MF, and GP. The reader should note that the notation and units previously adopted by this industry are primarily employed in the development.

REVERSE OSMOSIS

The most widely commercialized membrane process by far is reverse osmosis (RO), which belongs to a family of pressure driven separation operations for liquids that includes reverse osmosis, ultrafiltration, and microfiltration. Care should be exercised

here since some terms are used interchangeably. For example, RO is considered by some as hyperfiltration.

Reverse osmosis is an advanced separation technique that may be used whenever low molecular weight solutes such as inorganic salts or small organic molecules (e.g., glucose) are to be separated from a solvent (usually water). In normal (as opposed to reverse) osmosis, water flows from a less concentrated salt solution to a more concentrated salt solution as a result of an inate driving force (the aforementioned chemical potential). As a result of the migration of water, an "osmotic pressure" is created on the side of the membrane to which the water flows. In reverse (as opposed to normal) osmosis, the membrane is permeable to the solvent or water and relatively impermeable to the solute or salt. In order to make water pass through an RO membrane in the desired direction (i.e., away from a concentrated salt solution), a pressure must be applied that is higher than the osmotic pressure.

Reverse osmosis is widely utilized today by a host of industries for a surprising number of operations. Aside from the classic example of RO for seawater desalination, it has found a niche in the food industry for concentration of fruit juices, in the galvanic industry for concentration of waste streams, and in the dairy industry for concentration of milk prior to cheese manufacturing.[3–5] A more novel use of reverse osmosis is the production of low-alcohol beer by breweries in Denmark, France, and Germany. Reverse osmosis processes are classified into the following two basic categories:

1. Purification of a solvent such as in desalination where the *permeate* or purified water is the product.
2. Concentration of the solute such as in concentration of fruit juices where the *retentate* is the product.

The membranes used for RO processes are characterized by a high degree of semipermeability, high water fluxes, mechanical strength, chemical stability, and relatively low operating and capital costs. Early RO membranes were composed of cellulose acetate, but restrictions on process stream pressure, temperature, and organic solute rejection spurred the development of non-cellulosic and composite materials (membrane "sandwiches").

Reverse osmosis membranes may be configured into certain geometries for system operation: plate and frame, tubular, spiral wound (composite), and hollow fiber. These are detailed in the next paragraph.[5]

In the plate and frame configuration, flat sheets of membrane are placed between spacers with heights of approximately 0.5–1.0 mm. These are, in turn, stacked in parallel groups. Tubular units are also used for RO. This is a simpler design in which the feed flows inside of a tube whose walls contain the membrane. These types of membranes are usually produced with inside diameters of 12.5–25 mm. Also, they are generally made in lengths of 150–610 cm. There is also the hollow fine fiber (HFF) arrangement. This geometry is used in 70% of worldwide desalination applications. Millions of hollow fibers are oriented in parallel and fixed in epoxy at both ends. The feed stream is sent through a central distributor where it is forced out radially through the fiber bundle. As the pressurized feed contacts the fibers, the permeate is

forced into the center of each hollow fiber. The permeate then moves along the hollow bore until it exits the permeator. A spiral wound cartridge is occasionally employed. In this configuration, the solvent is forced inward towards the product tube while the concentrate remains in the spacing between the membranes. A flat film membrane is made into a "leaf." Each leaf consists of two sheets of membrane with a sheet of polyester tricot in between to act as a collection channel for the product water. Plastic netting is placed between each leaf to serve as a feed channel. Each leaf is then wrapped around the product tube in a spiral fashion.

Water covers around 70% of the Earth's surface but 97.5% of it is unfit for human consumption. With the world facing a growing fresh water shortage, from which the United States will not be spared, one method for producing fresh water that has been around for decades is *desalination*. Until recently, a thermal process was used to separate water from salt. Saline water was boiled until it evaporated, leaving the salt behind; the salt-free water is then reclaimed when the steam condensed. Unfortunately, it is a very expensive method because it requires significant amounts of energy. The technology of choice today is RO. Essentially, water is pumped under high pressure through membranes that filter off the salt. It too requires energy but not nearly as much as the thermal method. Recent advances in membrane technology and energy recovery methods have made the RO desalination process much more cost-competitive.

Thus, the major application of RO is water desalination. Areas of the world that do not have a ready supply of fresh water may choose to desalinate seawater or brackish water using RO to generate potable drinking water. Because no heating or phase change is required, the RO process (often referred to as hyperfiltration) is a relatively low energy water purification process. A typical salt water RO system consists of an intake, a pre-treatment component, a high-pressure pump, membrane apparatus, remineralization and pH adjustment components, as well as a disinfection step. Generally, a pressure of about 1.7–6.9 MPa is required to overcome the osmotic pressure of salt water.[2]

The wine and juice industries have applications for hyperfiltration as well. Flavor tests have shown positive results indicating the potential of membrane processing for improving taste. Using membranes with pore sizes controlled within a specific range has resulted in bitterness and "off-flavors" being removed from finished wine products as well as grapefruit and orange juice. After using a RO process, a taste-testing panel found a low quality Chenin Blanc to have a significantly better taste.[2] However, this is a difficult application as desirable and undesirable taste elements have a similar molecular size along with steric and polar characteristics that are also similar.

Another important application of hyperfiltration is the aforementioned dialysis. This technique is used in patients who suffer from kidney failure and can no longer filter waste products (urea) from the blood. In general, RO equipment used for dialysis can reduce ionic contaminants by up to 90%. In this process, the patient's blood flows in a tubular membrane while a dialysate flows countercurrently on the outside of the feed tube. The concentrations of undesirables such as potassium, calcium and urea are high in the blood and low or absent in the dialysate. Although this treatment successfully mimics the filtration capabilities of the kidney, it cannot replace its endocrine functionality.[1]

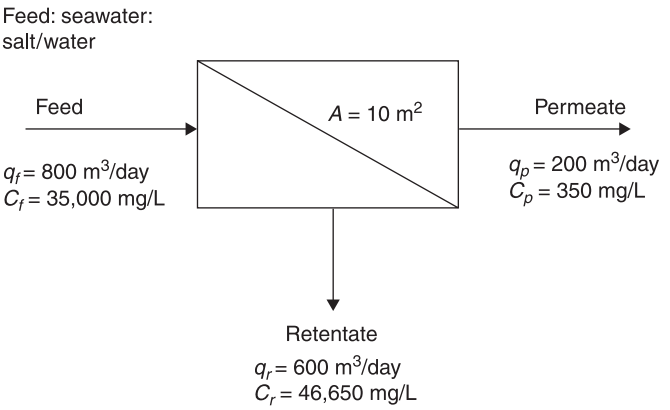

Figure 15.1 Seawater desalination by RO.

The membrane operation that incorporates a selective barrier can be reviewed using the process line diagram provided in Figure 15.1 for the purification of seawater. This membrane operation typifies the case where a feed stream (seawater) is separated by a semi-permeable membrane that rejects salt but selectively transports water. A purified water stream (the permeate) is therefore produced while, at the same time a concentrated salt stream (the retentate) is discharged. With reference to Figure 15.1, a simple material balance can be written on the overall process flows and for that of the solute:

$$q_f = q_r + q_p; \qquad q = \text{volumetric flow rate} \tag{15.1}$$

$$C_f q_f = C_r q_r + C_p q_p; \quad C = \text{solute concentrate} \tag{15.2}$$

Subscripts f, r, and p refer the feed, retentate, and permeate, respectively.

ILLUSTRATIVE EXAMPLE 15.1

Verify that the quantities provided in Figure 15.1 satisfy both a componential and overall material balance.

***SOLUTION*:** An overall balance yields (in m^3/day)

$$q_f = q_r + q_p$$
$$800 = 600 + 200$$
$$800 = 800$$

A componential balance on the salt gives (in mg/day)

$$(3500)(800)(1000) = (46{,}650)(600)(1000) + (350)(200)(1000);\ 1000\ \text{L} = 1\ \text{m}^3$$
$$2.80 \times 10^8 = 2.80 \times 10^8$$

Both balances are satisfied. ■

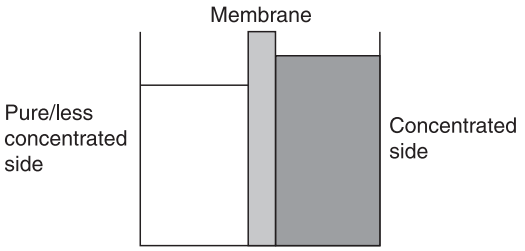

Figure 15.2 Before osmosis equilibrium.

Osmosis must first be better explained in order to fully describe RO. As previously mentioned, osmosis occurs when a concentrated solution is partitioned from a pure solute or a relatively lower concentration solution by a semi-permeable membrane. The semi-permeable membrane only allows the *solvent* to flow through it freely. Equilibrium is reached when the solvent from the lower concentration side ceases to flow through the membrane to the higher concentration side (thus reducing the concentration) because the mass transfer driving force has been "quenched". This is shown in Figures 15.2 and 15.3.

Osmotic pressure is termed as the pressure needed to stop the flux of solvent through the membrane or the force that pushes up on the concentrated side of the membrane (see Fig. 15.4). Applying a pressure on the concentrated side stops the solvent flux. Reverse osmosis (Fig. 15.5) takes place when an applied force (pressure)

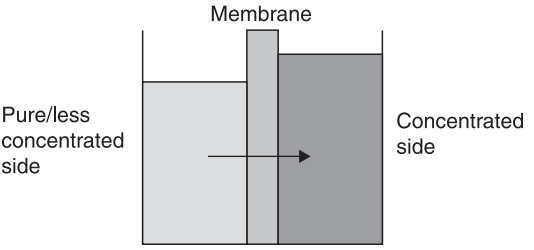

Figure 15.3 Osmosis of solvent.

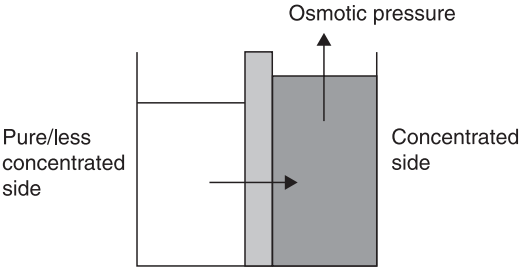

Figure 15.4 Osmotic pressure.

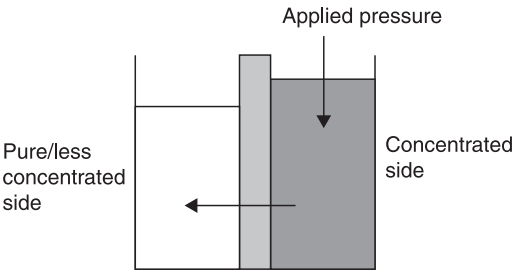

Figure 15.5 Reverse osmosis.

on the concentrated side overcomes the osmotic pressure and forces the solvent from the concentrated side through the membrane and leaves the solute on the concentrated side.

As noted above, osmotic pressure occurs when two solutions of different concentrations (or a pure solvent and a solution) are separated by a semi-permeable membrane. In simplest terms, it means that the membrane is permeable to the solvent but not to the solute. The solvent molecules in the dilute phase have a higher chemical potential than the molecules in the concentrated phase. This difference in chemical potential causes a flow of solvent molecules from the dilute phase (high chemical potential) to the concentrated phase (low chemical potential). Flow of solvent molecules into the concentrated solution continues until osmotic equilibrium is reached, i.e., until the chemical potential of the solvent molecules in both phases are equal.

Summarizing, Figure 15.6 provides a more detailed pictorial representation of what happens on the surface of a membrane in RO. A concentrated solution enters as the feed and is separated with the assistance of the membrane and the filtered solvent

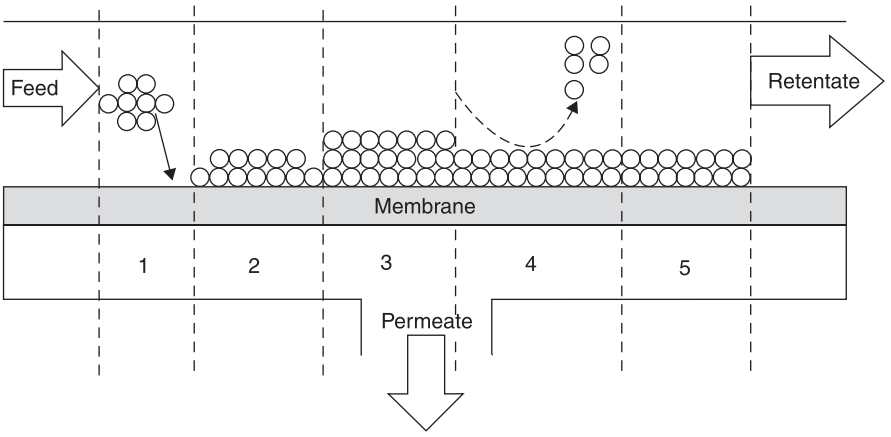

Figure 15.6 Explanation of what happens in a membrane process.

exits as the permeate. The retentate is the solvent that is not cleaned and is more concentrated than the feed solution. A step-by-step explanation (see Fig. 15.6) of this phenomenon follows:

1. The feed enters and the solution is forced to the surface of the membrane.
2. Some of the solvent passes through the membrane (not shown because it is smaller than solute) and some passes on to the retentate side.
3. The solute builds up a layer on the surface of the membrane, causing the flux to decrease (which reduces the quantity of feed being purified).
4. The feed solution that is still flowing comes into contact with the solute buildup on the membrane surface and removes some or even all of the solute on the membrane and re-entrains it in the flow to become the retentate. Downstream, the re-entrained solute can then be re-trapped on the surface of the membrane.
5. The whole process can be repeated with a small film on the membrane (where solute has been trapped already) or a totally clean part (downstream).

In the process, the retentate becomes more concentrated with the solute because the solute that is removed and trapped on the membrane becomes re-entrained by the tangential force of the feed solution that is still passing through the unit. The solvent is effectively forced through the membrane to make permeate (pure solvent) by the design of the filter itself.[6]

Reverse osmosis is the most selective of the three membrane processes described earlier that are used in industry for (primarily) liquid purification: microfiltration, ultrafiltration, and hyperfiltration. The three processes are shown schematically in Figure 15.7. In microfiltration, the particles to be concentrated are generally solids or colloids rather than molecules in solution. As previously stated, if there is a difference between RO and ultrafiltration; it is that the size of the particles or molecules to be separated in solution is smaller in RO. Various process flow schematics of RO are provided in Figure 15.8.[7]

Describing Equations

As noted above, one important characteristic of the RO process is the osmotic pressure of the solvent. Osmotic pressure is related to both the solute concentration and the temperature of the solution as described in the Van't Hoff equation below:

$$\pi = iC_sRT \tag{15.3}$$

where π = osmotic pressure, psi
i = Van't Hoff factor, dimensionless
C_s = solute concentration, mol/L
R = Universal gas constant, $L \cdot atm/mol \cdot K$
T = absolute temperature, K

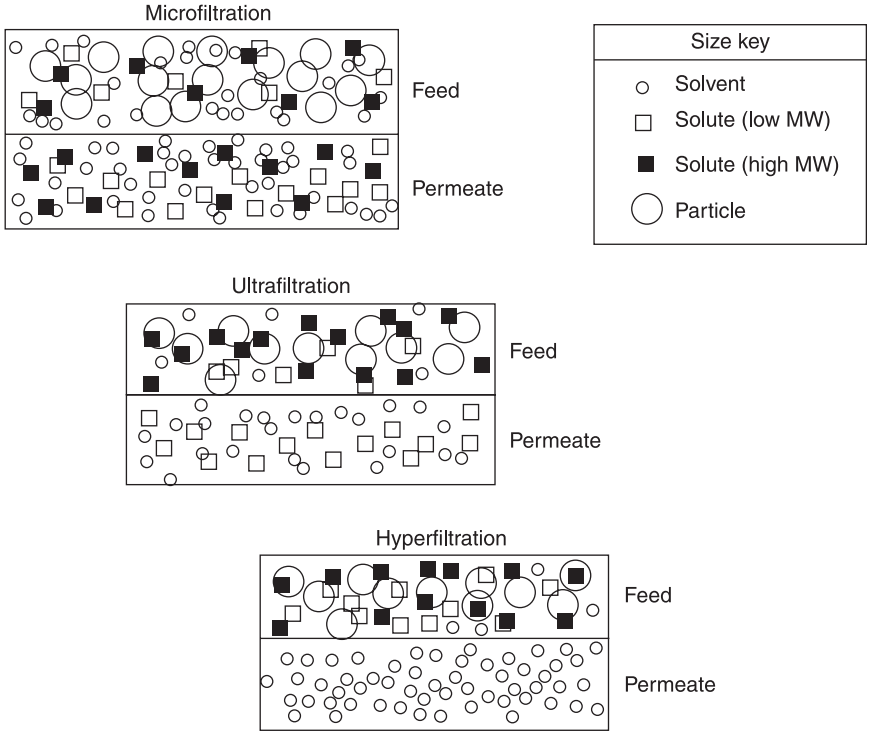

Figure 15.7 Membrane separation processes.

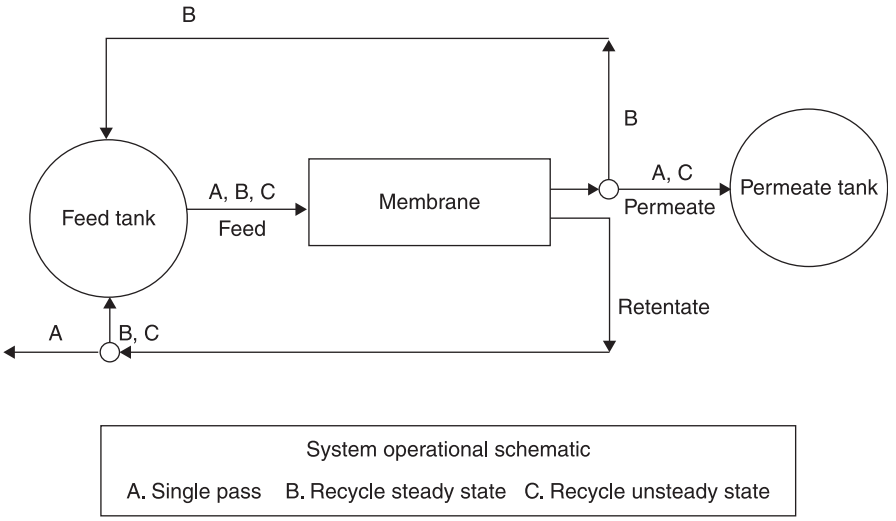

Figure 15.8 Process flow diagram (RO). (Adapted from C.S. Slater and J.D. Paccione, "A reverse osmosis system for an advanced separation process laboratory," *Chemical Engineering Education*, **22**, New York City, NY, pp. 138–143, 1987).

The Van't Hoff factor, i, takes into account the number of ions in solution. For example, NaCl separates into two ions, Na^+ and Cl^-, therefore making the Van't Hoff factor equal to 2. Upon closer inspection of Equation (15.3), one can readily observe that the Van't Hoff equation is analogous to the ideal gas law.

The change in osmotic pressure across the membrane in this operation must be overcome in order to achieve RO. This is shown by

$$\Delta\pi = \pi_f - \pi_p \tag{15.4}$$

where $\Delta\pi$ = change in osmotic pressure, psi
π_f = osmotic pressure in the feed, psi
π_p = osmotic pressure in the permeate, psi

This change in osmotic pressure can also be found using the concentrations of both the feed and the permeate, as well as a coefficient denoted as Ψ. This formula is shown by

$$\Delta\pi = \Psi(C_f - C_p) \tag{15.5}$$

where $\Delta\pi$ = osmotic pressure change, psi
Ψ = constant, $\mathrm{L \cdot psi/g}$
C_f = feed concentration, g/L
C_p = permeate concentration, g/L

The permeate flux is an important characteristic of the RO operation. It is related to the permeate flow as well as the area of the membrane. This can be seen in the following equation

$$J_p = \frac{q_p}{A_m} \tag{15.6}$$

where J_p = permeate flux, $\mathrm{gal/ft^2 \cdot day}$
q_p = permeate flow, gal/day
A_m = membrane surface area, $\mathrm{ft^2}$

The flux can be determined by measuring each incremental volume of permeate, ΔV, collected in time period Δt, and dividing by the surface area of the membrane. In water-based processes such as desalination, the permeate consists of mostly water. Therefore, the permeate flux can be considered to be equal to the water flux. Equation (15.7) defines the water flux:

$$J_p = J_w = A_w(\Delta P - \Delta\pi) = \frac{K_s}{t_m}(\Delta P - \Delta\pi) \tag{15.7}$$

where J_w = water flux, $\mathrm{gal/ft^2 \cdot day}$
J_p = permeate flux, $\mathrm{gal/ft^2 \cdot day}$
A_w = water permeability coefficient, $\mathrm{gal/ft^2 \cdot day \cdot psi}$

ΔP = pressure drop, psi
$\Delta \pi$ = osmotic pressure change, psi
K_s = permeability constant, gal/ft · day · psi
t_m = membrane thickness, ft

The water permeability coefficient can be experimentally determined by obtaining data on the unit with pure water; this eliminates the change in osmotic pressure since both sides of the membrane contain pure water.

Another important factor is the solute flux. This can be determined through the utilization of:

$$J_s = \frac{q_p C_p}{A_m} = \frac{\dot{m}_p}{A_m} \tag{15.8}$$

where J_s = solute flux, g/ft^2 · min
q_p = permeate flow rate, L/day
C_p = permeate concentration, g/L
$\dot{m}_p$ = permeate flow rate, g/day
A_m = membrane surface area, ft^2

The solute flux can also be related to the solute concentration by utilizing the solute permeability factor. This relationship is provided by

$$J_s = B_s(\Delta C_s) \tag{15.9}$$

where J_s = solute flux, g/ft^2 · min
B_s = solute permeability coefficient, L/ft^2 · min
ΔC_s = change in concentration, g/L

The selectivity of a membrane to filter out a solute can be expressed as the percent rejection (%R). Percent rejection represents a membrane's effectiveness and is a measure of the membrane's ability to selectively allow certain species to permeate and others to be rejected. This is an important characteristic when selecting a membrane for a separation process. The percent rejection represents the percentage of solute that was not allowed to pass into the permeate stream, and is given by

$$\%R = \left(\frac{C_f - C_p}{C_f}\right) \cdot 100\% \tag{15.10}$$

where %R = solute rejection, %
C_p = permeate concentration, g/L
C_f = feed concentration, g/L

Finally, the solvent recovery, Y, is a measure of how much solvent is allowed to pass through the membrane. This is defined as the quotient of the permeate flow

divided by the feed flow, as shown by

$$Y = \frac{q_p}{q_f} \tag{15.11}$$

where Y = solvent recovery, dimensionless–fractional basis
q_p = permeate flow, L/min
q_f = feed flow, L/min

ILLUSTRATIVE EXAMPLE 15.2

With reference to Figure 15.1, calculate the solvent flux and the membrane selectivity.

***SOLUTION*:** For the flux,

$$J_s = \frac{\dot{m}_s}{A_m} \tag{15.8}$$

Substituting,

$$J_s = \frac{200}{10} = 20\,\mathrm{m}^3/\mathrm{m}^2 \cdot \mathrm{day}$$

For the selectivity,

$$\%R = \left(\frac{C_f - C_p}{C_f}\right)100 \tag{15.10}$$

Substituting,

$$\%R = \left(\frac{35{,}000 - 350}{35{,}000}\right)100 = 99.0\%$$

■

The reader should note the following two basic membrane transport equations.

$$J = P\frac{(DF)}{t_m} \tag{15.12}$$

where J = flux
P = membrane permeability
DF = driving force across the membrane
t_m = membrane thickness

The driving force can be a pressure, concentration, or electric field. The flux, J, may also be written as

$$J = A_w(\Delta P - \Delta\pi) \tag{15.13}$$

where A_w = water or solvent permeability coefficient
ΔP = total pressure drop across the membrane
$\Delta\pi$ = osmotic pressure drop

ILLUSTRATIVE EXAMPLE 15.3

Consider the seawater desalination example discussed earlier. If the applied pressure gradient across the membrane is 500 psi and the membrane thickness is 10 μm, determine the permeability of the membrane in $m^2/s \cdot Pa$.

***SOLUTION*:** Employing Equation (15.12),

$$J = P\frac{(DF)}{t_m}$$

This equation may be rearranged and solved for P, being careful to employ consistent units,

$$P = \frac{Jt_m}{DF} = \frac{(20)(1/86{,}400)(10)(10^{-6})}{500(1.01325 \times 10^5/14.7)}$$
$$= 6.71 \times 10^{-16}\ m^2/s \cdot Pa$$

■

ILLUSTRATIVE EXAMPLE 15.4[1]

A new membrane material (#CSS-1) is to be evaluated for its solute and solvent permeability. A small test cell is utilized with a 5.0 cm diameter circular membrane. The test solution is 6000 mg/L of NaCl in water at 25°C. Assume that the following relationship holds for the osmotic pressure of NaCl in water (0.0114 psi/mg/L).

At an operating pressure gradient of 750 psi, the permeate flow rate is $0.0152\ cm^3/s$ and the permeate solute concentration is 150 mg/L. Assuming there is no concentration polarization and that the operating conditions remain constant, determine the water flux in $g/cm^2 \cdot s$ and the solute flux in $g/cm^2 \cdot s$.

***SOLUTION*:** The membrane surface area is

$$A_m = \frac{\pi(5)^2}{4} = 19.63\ cm^2$$

Employing Equation (15.8) for water,

$$J_w = \frac{\dot{m}_p}{A_m} = \frac{0.0152}{19.63} = 7.74 \times 10^{-4}\ g/cm^2 \cdot s$$

Noting that

$$\frac{C_p}{C_w} = \frac{J_s}{J_w}$$
$$J_s = \frac{C_p J_w}{C_w} = \frac{150}{10^6}(7.74 \times 10^{-4}) = 1.16 \times 10^{-7}\ g/cm^2 \cdot s$$

■

ILLUSTRATIVE EXAMPLE 15.5[1]

Refer to Illustrative Example 15.4. Calculate the percent solute rejection.

***SOLUTION*:** The percent rejection is given by Equation (15.10).

$$\%R = \left(\frac{C_f - C_p}{C_f}\right)100 = \left(\frac{6000 - 150}{6000}\right)100 = 97.5\%$$

■

ULTRAFILTRATION

Ultrafiltration (UF) is a membrane separation process that can be used to concentrate single solutes or mixtures of solutes. Trans-membrane pressure is the main driving force in UF operations and separation is achieved via a "sieving" mechanism. The UF process can be used for the concentration of oily wastewater, for pretreatment of seawater prior to RO, and for the removal of bacterial contamination (pyrogens). In the food industry, UF is used to separate lactose and salt from cheese whey proteins, to clarify apple juice, and to concentrate milk for ice cream and cheese production.[8–10] The most energy intensive step in ice cream production is the concentration of skimmed milk, where membrane processes are more economical for this step than vacuum evaporation.[9] UF processes are also used for the concentrating or dewatering of fermentation products, and for the purification of blood fractions and vaccines.

UF membranes are rated in terms of their molecular weight cutoff, thereby separating proteins and other biochemicals according to their molecular weight differences. Thin, mechanically strong, flexible, non-adsorbing, and flat-textured, UF membranes are available in a wide variety of cutoff sizes. For example, the YM-30 membrane (employed in a Manhattan College laboratory experiment) will retain any material with a MW $>$30,000. Most UF membranes have an asymmetric structure with a thin selective membrane supported by a thicker porous structure, which is the case for the YM-30 membrane.

Ultrafiltration may be thought of as a membrane separation technique where a solution is introduced on one side of a membrane barrier while water, salts, and/or other low molecular weight materials pass through the unit under an applied pressure. Membrane separation processes can be used to concentrate single solutes or mixtures of solutes. The variety in the different membrane materials makes a wide temperature/pH processing range possible.

The main economic advantage of UF is a reduction in design complexity and energy usage since UF processes can simultaneously concentrate and purify process streams. The fact that no phase change is required leads to highly desirable energy savings. Also, as no catalysts are needed for these separations or chemical reagents required, there are further operational savings. A major disadvantage is the high capital investment that might be required if low flux rates for purification demand a large system design. However, UF processes stand out as economically sound in comparison to other traditional separation techniques.

In addition to the application decribed above, ultrafiltration membrane processes are utilized in various commercial applications. They are found in the treatment of industrial effluents and process water, concentration, purification, and separation of macromolecular solutions in the chemical, food, and drug industries; sterilization,

clarification, and prefiltering of biological solutions and beverages; and, production of ultra pure water and preheating of sea water in RO processes.

The most promising area for the expansion of UF process applications is in the biochemical area. Some of its usage in this area includes purifying vaccines and blood fractions; concentrating gelatins, albumin, and egg solids; and, recovering proteins and starches.

Ultrafiltration processes have also been used in the production of leukocyte interferon from white blood cells and fibroblast interferon from cell culture, and for the production of human insulin. Usage of the leukocyte interferon includes the treatment of chronic viral hepatitis in heart transplant recipients.

Ultrafiltration is an effective purification and concentration process for enzymes. Processes to concentrate and purify enzymes are becoming increasingly important to the biochemical industry where UF is typically employed in downstream separation and recovery of fermentation products.

Ultrafiltration of milk is also an important industrial process with the retentate of thickened milk product used in the manufacture of cheese and other milk products. A polysulfone membrane with a 20,000 MWCO (molecular weight cutoff) is normally employed.

At low temperatures and pressures, ultrafiltration separates high molecular weight components from the lower molecular weight ones. It allows the lower molecular weight components to permeate along with water. The molecular weight cutoff of a membrane might be defined, for example, as the molecular weight that is 90% rejected by the membrane which indicates that a 10,000 MWCO membrane will reject 90% of solutes having a MW of more than 10,000 Daltons (1 Da = 1 amu).

The rejection of a solute is a function of the size, size distribution, shape, and surface binding characteristics of the hydrated molecule. It is also a function of the pore-size distribution of the membrane and therefore molecular weight cutoff values can only be used as a rough guide for membrane selection. The retention efficiency of the solutes depends to a large extent on the proper selection and condition of membranes. Replacement of highly used membranes and regular inspections of the separation units averts many problems that would otherwise occur because of clogging and gel formation.

Describing Equations

The general design factors for any membrane system (including UF) are reported by Wankat as:[11]

1. Thin active layer of membrane
2. High permeability for species A and low permeability for species B
3. Stable membrane with long service life
4. Mechanical strength
5. Large surface area of membrane in a small volume
6. Concentration polarization elimination or control

7 Ease in cleaning, if necessary

8 Inexpensive to build

9 Low operating costs

System performance is usually defined in terms of permeate flux, J_p, with dimensions of volume/area · time. The typical units are $L/m^2 \cdot h$. As with RO, J_p can be obtained experimentally by measuring the incremental volume of the permeate, ΔV, collected in a time period, Δt. Thus, the permeate flux describing equation is

$$J_p = \frac{\Delta V/\Delta t}{\text{surface area}} \tag{15.14}$$

where J_p = permeate flux, $L/m^2 \cdot h$

ΔV = incremental volume of permeate, m^3

Δt = collection time period, h

Surface area = surface area of the membrane, m^2

Other consistent units for the flux may be employed, for example, $cm^3/cm^2 \cdot s$.

Trans-membrane pressure is the main driving force in UF operations, and separation is achieved through the aforementioned sieving mechanism. Since UF is a pressure-driven separation process, it is appropriate to examine the effects of pressure on flux. Equation (15.15) shows how the flux varies with pressure. It is seen that the flux of a pure solvent through a porous membrane is directly proportional to the applied pressure gradient across the membrane, ΔP, and inversely proportional to the membrane thickness, t_m:

$$J_s = \frac{K_s}{t_m}(\Delta P - \Delta \pi) \tag{15.15}$$

where K_s = permeate constant, $cm^2/psi \cdot s$

ΔP = pressure drop across the membrane (trans-membrane pressure), psi

$\Delta \pi$ = osmotic pressure difference across the membrane, psi

t_m = membrane thickness, cm

Such factors as the membrane porosity, pore size distribution, and viscosity of the solvent are accounted for by the permeability constant, K_s. When t_m is not available or is not known, the water permeability coefficient, A_w, may be used in place of K_s. The water permeability coefficient is a function of the distribution coefficient (solubility), diffusion coefficient, membrane thickness, and temperature. The value of A_w can be determined by conducting ultrapure water-flux experiments at varying operating pressures while the permeate collection occurs at atmospheric pressure.

The osmotic pressure is relatively low for macromolecular solutions, which are typically the ones recommended for UF processes, and therefore the $\Delta \pi$ term can be neglected in Equation (15.15). This is the case since the molar concentration of the high molecular weight molecules separated by UF is quite low, even when the

mass concentrations are high. When the $\Delta\pi$ term is neglected and K_s/t_m is replaced with A_w, the following equation is obtained:

$$J_s = A_w \Delta P \tag{15.16}$$

where A_w = water permeability coefficient, $cm^2/psi \cdot s$.

When a solute such as milk solids dissolved in water flows through a typical UF process, some of the solute usually passes through the membrane since real membranes are partially permeable. The *apparent rejection* on a fraction basis is then once again calculated as follows (see also Eq. 15.10):

$$R_{app} = \frac{C_r - C_p}{C_r} \tag{15.17}$$

where R_{app} = apparent rejection, dimensionless–fractional basis
C_p = permeate concentration, g/cm^3
C_r = retentate concentration, g/cm^3

There are three important factors that need to be considered in UF separations: *concentration polarization*, *gel formation*, and *fouling*. A concentration gradient or boundary layer typically forms during a UF process. This concentration gradient appears near the membrane surface and is referred to as concentration polarization. It results from the counteracting effects of the convective flow of solute towards the membrane and diffusion of the solute back toward the bulk fluid. While concentration polarization is regarded as a reversible boundary-layer phenomenon that causes a rapid initial drop in flux to a steady-state value, fouling is considered as an irreversible process that leads to a flux decline over the long term. Gel formation, however, may be reversible or irreversible. When the gel is difficult to remove, the membrane is said to be fouled and thus the gel formation is irreversible. Concentration polarization may occur with or without gel formation.

Concentration polarization occurs in many separations, and for large solutes where osmotic pressure can be neglected, concentration polarization without gelling is predicted to have no effect on the flux. Therefore, if a flux decline is observed, it can be attributed to the formation of a gel layer with a concentration C_g. The gel layer, once formed, usually controls mass transfer so that Equation (15.15) is no longer applicable. When this happens, Equation (15.18) can be used to determine the solvent flux:

$$J = \frac{\Delta P}{R_m + R_g} \tag{15.18}$$

where R_m = resistance to flow through the membrane, $psi \cdot s \cdot cm^2/cm^3$
R_g = resistance to flow through the gel, $psi \cdot s \cdot cm^2/cm^3$

The value of R_g varies with pressure, bulk concentration, and cross-flow velocity at lower transmembrane pressure, but tends to become pressure independent at higher transmembrane pressures. This value can be, and often is, measured experimentally.

When the gel layer controls mass transfer and $C_p = 0$ or the apparent rejection is unity, the solvent flux can be expressed in terms of a mass transfer coefficient, k, as follows:

$$J_s = k \ln\left(\frac{C_g}{C_r}\right) \tag{15.19}$$

where C_g = gel layer concentration, g/cm^3
k = mass transfer coefficient, cm^3/cm$^2 \cdot$ s

To determine an experimental value for k, data can be measured when $R \approx 1$, for the flux as a function of the bulk concentration. This information can be graphed using Equation (15.20) which is a rearrangement of Equation (15.19) above. This plot is obtained for a constant temperature and cross-flow velocity. A plot of J_s vs ln C_g on arithmetic coordinates has a slope of $-k$ and the y-axis intercept is the ln (natural log) of C_g,

$$J_s = \ln C_g - k \ln C_b \tag{15.20}$$

Empirical equations can be employed in the determination of the mass transfer coefficient, k. Fully developed turbulent flow in UF devices appears to occur at Re$\geq$2000. The Reynolds number can be calculated using an equivalent diameter as follows:

$$D_{eq} = 4\left(\frac{\text{cross-sectional area}}{\text{wetted perimeter}}\right) = 4\left(\frac{2hw}{2w + 4h}\right) \tag{15.21}$$

where w = width of the channel, mm
h = height of the channel, mm (the channel height is usually defined as $2h$ rather than h)

The following equation can be used to determine the mass transfer coefficient for turbulent flow through a channel:

$$k = 0.023 \frac{D}{D_{eq}} \text{Re}^{0.83} \text{Sc}^{1/3} \tag{15.22}$$

where

$$\text{Re} = \frac{D_{eq} u_b \rho}{\mu} \quad \text{and} \quad \text{Sc} = \frac{\mu}{D\rho} \tag{15.23}$$

where u_b = linear velocity through the channel, m/s
D = diffusivity, m^2/s
μ = viscosity, kg/m $\cdot$ s
ρ = density, kg/m^3

The above physical properties are based on the average concentration of the fluid on the feed side of the membrane. The density is estimated on a weight percent solids basis.

For laminar flow through a channel, the average mass transfer coefficient can be estimated using the following equation:

$$k = 1.177\left[\frac{u_b D^2}{hL}\right]^{1/3} \tag{15.24}$$

where L = length of the flow channel, mm

This correlation is used when the concentration polarization is thin, which holds when the axial distance is much less than the entrance length.

Energy costs need to be considered. It has been found that the energy costs for the laminar flow system are generally lower, and thus it is normally the desirable mode of operation.

ILLUSTRATIVE EXAMPLE 15.6

Determine the volume of milk solution and water to be mixed in order to produce a total of 400 ml for a 1 : 8 milk to water volume ratio.

***SOLUTION*:**

$$\text{Amount of milk} = \left(\frac{1}{1+8}\right)400\,\text{ml} = 44.4\,\text{ml}$$

$$\text{Amount of water} = \left(\frac{8}{1+8}\right)400\,\text{ml} = 355.6\,\text{ml}$$ ■

ILLUSTRATIVE EXAMPLE 15.7

During a 12 psi UF run with pure water, the incremental volume of water collected for a 580 s time interval was 50 cm^3. If the effective surface area is 40 cm^2, calculate the permeate flux.

***SOLUTION*:** Apply Equation (15.14):

$$J_p = \frac{\Delta V/\Delta t}{A_m}$$

The permeate flux is therefore found to be

$$J_p = \frac{50\,\text{cm}^3/580\,\text{s}}{40\,\text{cm}^2} = 0.002155\text{cm}^3/\text{cm}^2 \cdot \text{s}$$ ■

ILLUSTRATIVE EXAMPLE 15.8

The average concentration of the retentate for a UF run is 1.117 g/cm^3. If a 19 cm^3 permeate sample is placed on a 1.0534 g tray and dried to a weight of 1.1454 g, calculate the apparent rejection.

***SOLUTION*:** The apparent rejection, R_{app} is determined as follows:

$$R_{app} = \frac{C_r - C_p}{C_r} \tag{15.17}$$

The permeate concentration is found using the data provided:

$$C_p = \frac{(1.1454 - 1.0534)\,\text{g}}{19\,\text{cm}^3} = 0.00484\,\text{g/cm}^3$$

The apparent rejection is therefore

$$R_{app} = 1 - \frac{0.00484\,\text{g/cm}^3}{1.117\,\text{g/cm}^3} = 0.9957$$
$$= 99.57\%$$

■

ILLUSTRATIVE EXAMPLE 15.9

The mass transfer coefficient can be estimated from empirical equations. The empirical equation used depends on whether the flow is laminar or turbulent. The Reynolds number needs to be calculated to determine the type of flow. Consider the following UF bench scale system and operating conditions. The height and width of the channel available for flow are 0.038 and 0.95 cm, respectively. The average velocity in the channel is 0.116 cm/s and the flowing fluid's density and viscosity have been estimated to be 1.013 g/cm^3 and 0.020 g/cm · s, respectively. Calculate the Reynolds number.

***SOLUTION*:** The equivalent diameter D_{eq} can be estimated from Equation (15.21)

$$D_{eq} = 4\left(\frac{\text{cross-sectional area}}{\text{wetted perimeter}}\right) = 4\left(\frac{2hw}{2w + 4h}\right)$$

Substituting

$$D_{eq} = 4\left(\frac{2(0.00038)(0.0095)}{2(0.0095) + 4(0.00038)}\right)$$
$$= 0.00146\,\text{m}$$

The Reynolds number can now be estimated from Equation (15.23).

$$\text{Re} = \frac{(0.146\,\text{cm})(0.116\,\text{cm/s})\left(1.0127\,\text{g/cm}^3\right)}{(0.02\,\text{g/cm} \cdot \text{s})} = 0.8576$$

The flow is therefore laminar. ■

ILLUSTRATIVE EXAMPLE 15.10

Refer to the previous illustrative example. Calculate the mass transfer coefficient. The length of the channel is 41.4 cm.

***SOLUTION*:** The flow is laminar. For a laminar flow through a channel, the mass transfer coefficient can be calculated using Equation (15.24)

$$k = 1.177\left[\frac{u_b D^2}{hL}\right]^{1/3}$$

where D is the diffusivity. The calculation for k cannot be completed since D is not specified. If the system is lactose in water, the diffusivity is approximately $4.9 \times 10^{-10}\text{m}^2/\text{s}$. Substituting into the above equation (maintaining dimensional consistency)

$$\begin{aligned} k &= 1.177\left[\frac{(0.00116\,\text{m/s})\left(4.9 \times 10^{-10}\,\text{m}^2/\text{s}\right)^2}{(0.00038\,\text{m})(0.414\,\text{m})}\right]^{1/3} \\ &= 1.424 \times 10^{-6}\,\text{L/m}^2 \cdot \text{h} \\ &= 1.424 \times 10^{-6}\,\text{m}^3/\text{m}^2 \cdot \text{s} \\ &= 1.424 \times 10^{-3}\,\text{L/m}^2 \cdot \text{s} \\ &= 5.126\,\text{L/m}^2 \cdot \text{h} \end{aligned}$$

■

MICROFILTRATION

Microfiltration (MF) is employed in modern biochemical and biological separation processes. For example, in cell harvesting, microfiltration can be used instead of centrifugation or pre-coat rotary vacuum filtration to remove yeast, bacteria, or mycelial organisms from fermentation broth. Both MF and UF are used for cell harvesting. Microfiltration is used to retain cells and colloids, while allowing passage of macromolecules into the permeate stream. Ultrafiltration is used to concentrate macromolecules, cells, and colloidal material, while allowing small organic molecules and inorganic salts to pass into the permeate stream. Pore sizes in microfiltration are around 0.02–10 μm in diameter as compared with 0.001–0.02 μm (300–300,000 Daltons) for ultrafiltration (ranges vary slightly depending on the source).[12,13]

Similar types of equipment are used for MF and UF, but membranes with larger pore sizes are installed in MF applications. MF and UF belong to a group of separation processes that depend on pressure as the driving force for separation. MF processes operate at lower pressures than UF, but at higher pressures than conventional particulate filtration. Ideal membranes possess high porosity, a narrow pore size distribution, and a low binding capacity. When separating microorganisms and cell debris from fermentation broth, a biological cake is formed. Principles of cake filtration apply to MF systems except that the small size of the yeast particles results in a cake with a relatively high resistance to flow and a relatively low filtration rate.

In dead-end filtration, feed flow is perpendicular to the membrane surface, and the thickness of the cake layer on the membrane surface increases with filtration time; consequently, the permeation rate decreases. Cross-flow filtration, on the other hand, features feed flow parallel to the membrane surface, which is designed to decrease formation of a cake layer by sweeping previously deposited solids from the membrane surface and returning them to the bulk feed stream. Cross-flow filtration is far superior

to dead-end filtration for cell harvesting because the biological cake is highly compressible, which causes the accumulated layer of biomass to rapidly blind the filter surface in dead-end operation. Therefore, MF experiments are often conducted using cross-flow filtration because of the advantages that this mode offers.[14,15]

In addition to the mode of operation and cross-flow rate, a number of other factors affect system performance including the following:

1. Operating Temperature: Temperature affects the viscosity of the feed suspension, and subsequently affects permeate flux through both the membrane and the biological cake. Viscosity decreases as temperature increases; hence, it is desirable to operate at the highest temperature that can be tolerated by the species being separated, and the membrane material being used.
2. Average Transmembrane Pressure (ATP): ATP is the average pressure on the retentate side of the membrane minus the average pressure on the permeate side. Increased operating pressure increases permeate flux for ultrapure water but tends to compact biomass on the membrane surface in MF processes. For yeast slurries, increased ATP should increase the transient flux but it may increase, decrease or have little effect on final steady-state fluxes depending on cake compressibility.
3. Yeast Concentration in the Feed: Permeate flux is inversely related to feed concentration, i.e., the final steady-state flux values decrease as the yeast concentration increases. Also, transient fluxes decline faster at higher concentrations because of accelerated cake buildup.
4. pH: The pH of the feed suspension affects the binding characteristics of the membrane and solubility of macromolecules, which in turn influences membrane fouling. The flux should vary inversely with pH.
5. Feed Preparation: Redkar and Davis[16] report that steady-state fluxes for slurries of unwashed Fleischmann's yeast are significantly lower than fluxes observed when the yeast is washed prior to preparing the feed suspension. Differences are attributed to the presence of extracellular proteins and other macromolecules in the unwashed yeast suspensions, factors that tend to increase specific cake resistance.

Describing Equations

Separation principles and governing equations for MF are similar to that for RO and UF. This presentation is primarily directed toward the theoretical aspects of MF. System performance is usually defined in terms of permeate flux, J_p, with dimensions of (volume/area · time), i.e., typical units are $L/m^2 \cdot h$. As noted earlier, the flux can be determined by measuring each incremental volume of permeate, ΔV, collected in time period, Δt, and dividing by surface area of the membrane as follows:

$$J_p = \frac{\Delta V/\Delta t}{\text{surface area}} \tag{15.25}$$

Since MF is a pressure-driven separation process, it is appropriate to comment on the effects of pressure on flux. Flux of a liquid solution through a porous membrane is directly proportional to the applied pressure gradient across the membrane, ΔP, and inversely proportional to the solution viscosity, μ, and membrane thickness, t_m (see Equation 15.26):

$$J_s = \frac{K_s \Delta P}{t_m} = \frac{\Delta P}{\mu R_m} \tag{15.26}$$

The hydrodynamic resistance of the membrane, R_m, is inversely related to the solvent permeability constant, K_s. The permeability constant accounts for factors such as membrane porosity, pore size distribution, and viscosity of the liquid. Permeate is normally collected at atmospheric pressure.

In membrane separation processes with pure solvent, temperature effects on flux generally follow the Arrhenius relationship where J_o is the flux at 25°C, E_a is the activation energy, R is the universal gas constant, and T is absolute temperature.

$$J_s = J_o e^{(E_a/RT)} \tag{15.27}$$

Equation (15.27) may also be written as:

$$\ln(J_s) = \ln(J_o)\left(\frac{E_a}{R}\right)\frac{1}{T} \tag{15.28}$$

Changes in flux with temperature result from changes in solution viscosity. As previously stated, viscosity decreases as temperature increases; thus, water permeability through the membrane subsequently increases. This relationship can be shown to hold for a Newtonian fluid like distilled water. Fermentation broth containing suspended microorganisms is a non-Newtonian fluid; therefore, increased temperatures tend to improve flux but not to the same magnitude as observed with dilute aqueous solutions.

It can be seen from Equation (15.26) that the product of $(J_s\mu)$ should be a constant value in temperature studies on water at constant ΔP. Substituting Equation (15.26) into (15.27) and taking the logarithm of both sides of the resultant equation leads to the Arrhenius-type relationship similar to Equation (15.28). Thus, if one employs ultrapure water at varying temperatures and constant transmembrane pressure, E_a can be determined from the slope of a graph of $\ln(1/\mu)$ vs $1/T$,

$$\ln\left(\frac{1}{\mu}\right) = \ln\left(\frac{1}{\mu_o}\right) - \left(\frac{E_a}{R}\right)\frac{1}{T} \tag{15.29}$$

The primary factor limiting flux in MF processes is cake buildup. Fouling, caused by factors such as proteins being adsorbed on the membrane surface and increased cake resistance because of cell debris, antifoam, precipitates, etc., which fill the void space in the biological cake, may also contribute to the flux decline.

As noted above, cross-flow filtration is designed to sweep the membrane surface so as to sweep deposited solids off of the membrane surface. Cross-membrane flow rate can be varied and its effect on flux determined. While the cross-flow mode is a significant improvement over dead-end filtration, the permeate flux still decreases to

some steady-state value of limiting flux, J_∞. The limiting flux can be modeled in terms of the resistances to permeation through the membrane, R_m, the biological cake, R_c, and the gel or fouling layer, R_g, as follows:

$$J_\infty = \frac{\Delta P}{\mu(R_m + R_c + R_g)} \tag{15.30}$$

The resistances in Equation (15.30) can be measured experimentally. For example, the value of R_m can be found by initial clean water flux measurements (Equation 15.26). The total resistance $(R_m + R_c + R_g)$ is measured from the final steady-state flux through the system after cake buildup, e.g., with yeast slurry as feed. After completing yeast runs, the MF system may be cleaned in two steps:

1. cleaning with water to remove yeast cake and other reversible deposits, and
2. chemical cleaning with a solution (e.g., hypochlorite) to remove fouling deposits.

After cleaning with water, the value for $(R_m + R_g)$ is measured by clean water fluxes. As R_g is usually negligible in microfiltration processes, thorough cleaning with water should result in flux values that are very close to the original water values. Therefore, chemical cleaning should not be required under normal operating conditions but may be required if membranes are to be reused after high pressure or low cross-flow studies.

The final concentration of the retentate (e.g., yeast cells), C_r, can be used as an absolute measure of system performance. A relative measurement of performance would be the concentration factor, ψ, defined as the ratio of the initial feed volume, V_0, to the final retentate volume, V_r, i.e., $\psi = V_0/V_r$. Initial and final volumes and concentrations can also be used to calculate the recovery, Y, where C_0 is the initial cell concentration in the feed.

$$\text{Recovery, } Y = \frac{(C_r)(V_r)}{(C_0)(V_0)} \times 100\% \tag{15.31}$$

Solute rejection, R^o, is another parameter that can be used to measure performance in these systems[17] where C_p is the concentration of yeast cells in the permeate. This parameter is given by:

$$R^o = 1 - (C_p/C_0) \tag{15.32}$$

ILLUSTRATIVE EXAMPLE 15.11

The data corresponding to a pressure run of 1.5 psi in a MF resulted in a flux for the pure water system of 196.7 $\text{mL/m}^2 \cdot \text{s}$. Calculate the membrane hydrodynamic resistance (R_m).

***SOLUTION*:** When converted to the "proper" units, the value of the flux is

$$J = 708\,\text{L/m}^2 \cdot \text{h}$$

R_m is calculated using the following formula:

$$R_m = \frac{\Delta P}{J_p \mu} \tag{15.26}$$

For water at 25°C:

$$\begin{aligned}\mu &= 3.60\ \text{kg/m} \cdot \text{h} \\ &= 0.001\ \text{kg/m} \cdot \text{s}\end{aligned}$$

Substituting gives

$$R_m = \frac{1.5}{(708)(3.60)} = 5.89 \times 10^{-4}\ \text{psi} \cdot \text{m}^3 \cdot \text{h}^2/\text{L} \cdot \text{kg}$$

The reader is left the exercise of converting the above results to units of $\text{m} \cdot \text{h}^2/\text{L}$. (The answer is 0.173). ■

ILLUSTRATIVE EXAMPLE 15.12

Refer to Illustrative Example 15.11. Calculate the cake resistance if fouling is neglected. Assume the steady-state (or limiting) flux value to be approximately half the value calculated in the previous example.

***SOLUTION*:** The cake resistance is calculated using the following formula:

$$J_\infty = \frac{\Delta P}{\mu(R_m + R_c)}; \quad (R_g = 0.0) \tag{15.30}$$

When rearranging to solve for the cake resistance, the following formula is obtained:

$$R_c = \frac{\Delta P}{J_\infty \mu} - R_m; \quad \Delta P = 1.5\,\text{psi} = 440\,\text{kg}_\text{f}/\text{m}^2$$

Substituting the values in the equation gives:

$$\begin{aligned}R_c &= \frac{440}{(3.6)(708/2)} - 0.173 \\ &= 0.172\ \text{m} \cdot \text{h}^2/\text{L}\end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 15.13

Data for a yeast run in a MF system yielded the following concentration–volume data over a 5 min sampling period:

C_r = final concentration of yeast cells in retentate = 0.5 g/L
C_o = initial cell concentration in feed = 1.2 g/L

V_r = final retentate volume = 290 L
V_o = initial feed volume = 150 L

Calculate the recovery.

***SOLUTION*:** The recovery of the system is calculated using the following formula:

$$Y = \frac{(C_r)(V_r)}{(C_o)(V_o)} \times 100\% \tag{15.31}$$

Substituting the values gives:

$$Y = \frac{(0.5)(2.9)}{(1.2)(1.5)} \times 100\%$$
$$= 80.56\% = 0.8056$$

■

ILLUSTRATIVE EXAMPLE 15.14

Refer to the previous example. Calculate the solute rejection, R^o, if the concentration of the yeast cells in the permeate is 0.10 g/L.

***SOLUTION*:** The solute rejection is calculated using the following formula:

$$R^o = 1 - (C_p/C_o) \tag{15.32}$$

Substituting the values gives:

$$R^o = 1 - (0.1/1.2)$$
$$= 0.92$$

■

GAS PERMEATION

Several different types of membrane separation processes are used in the chemical process industries, including systems for gas separation. These processes are generally considered as new and emerging technologies because they are not included in the traditional chemical engineering curriculum.[18–23]

The use of membranes in gas separation processes was commercialized by Monsanto in the early 1970s with the development of the hollow fiber Prism system for which the Monsanto Company won the 1981 Kirkpatrick Chemical Engineering Achievement Award. The hollow fiber membrane allowed, for the first time, the practical use of membranes in large-scale gas separation and purification processes. Several other firms, including UOP, Air Products and Chemicals, Dow, DuPont and Grace produce these gas permeation membrane units.[18]

Gas permeation systems have and continue to gain popularity in both traditional and emerging engineering areas. These systems were originally developed for hydrogen recovery. There are presently numerous applications of gas permeation in industry and other potential uses of this technology are in various stages of development. Applications include gas recovery from waste gas streams, landfill gases, and ammonia

and petrochemical products. Gas permeation membrane systems are also employed in gas generation and purification, including the production of nitrogen and enriched oxygen gases.[18]

Gas permeation is the term used to describe a membrane separation process using a non-porous semi-permeable membrane. In this process, a gaseous feed stream is fractionated into permeate and non-permeate streams. The non-permeating stream is typically referred to as the *non-permeate* in gas separation terminology and defined as the retentate in liquid separation. Transport occurs by a solution diffusion mechanism. Membrane selectivity is based on the relative permeation rates of the components through the membrane. Each gaseous component transported through the membrane has a characteristic permeation rate that depends on its ability to dissolve and diffuse through the membrane material. The mechanism for transport is based on solubilization and diffusion; the two describing relationships upon which the transport are based are Fick's law (diffusion) and Henry's law (solubility).[18]

Describing Equations

Diffusive flux through the membrane can be expressed by Fick's law, as related to the membrane system, and given by[18]

$$J_i = \frac{D_i}{t_m}(C_{im2} - C_{im1}) \tag{15.33}$$

where J_i = flux of component i, mole/m$^2 \cdot$ s

D_i = diffusivity of component i, m^2/s

t_m = thickness of the membrane, m

C_{im1} = concentration of component i inside membrane wall on feed side, mole/m^3

C_{im2} = concentration of component i inside membrane wall on permeate side, mole/m^3

Henry's law may be written in the following form[18]

$$C_{im} = S_i p_i \tag{15.34}$$

where S_i = solubility constant for component i in the membrane

p_i = partial pressure of component i in the gas phase

Substituting Equation (15.34) into Equation (15.33) yields[18]

$$J_i = \frac{D_i}{t_m}(S_i p_{i2} - S_i p_{i1}) \tag{15.35}$$

The terms p_{i2} and p_{i1} are the respective partial pressures of gas i on the feed and permeate side of the membrane. Permeation through the membrane is a function of solubility and diffusivity, as provided by[18]

$$P_i = D_i S_i \tag{15.36}$$

Substitution of Equation (15.36) into Equation (15.35) provides the relationship for local flux through the membrane[18]

$$J_i = \frac{P_i}{t_m}(p_{i2} - p_{i1}) \tag{15.37}$$

The separation efficiency a_{ij} is based on the different rates of permeation of the gas components:

$$a_{ij}^{*} = \frac{P_i}{P_j} \tag{15.38}$$

This data is available for some commonly separated gases and the polymer(s) used.[13,23]

An experimental separation factor a_{ij} is frequently used to quantify the separation of a binary system of components i (oxygen, O_2) and j (nitrogen, N_2), where C_p and C_r represent molar concentrations in the permeate and retentate (non-permeate) streams, respectively.[22] The separation factor can also be defined in terms of C_p and $C_{i,j}$, i.e., concentrations in the permeate and feed streams, respectively.[18,21] These relationships can be written in terms of mole fractions y_p, y_r, and y_f, which is often more convenient since (the oxygen) analyzers measure concentrations in mol%:[17]

$$a'_{ij} = \frac{C_{ip}/C_{jp}}{C_{ir}/C_{jr}} = \frac{y_{ip}/y_{jp}}{y_{ir}/y_{jr}} \tag{15.39}$$

$$a''_{ij} = \frac{C_{ip}/C_{jp}}{C_{if}/C_{jf}} = \frac{y_{ip}/y_{jp}}{y_{if}/y_{jf}} \tag{15.40}$$

Recovery is defined by the equations below, where q_p, q_r, and q_f represent the volumetric flow rates of the permeate, retentate (or non-permeate), and feed streams, respectively (m^3/s). Volumetric flow rates of the permeate and non-permeate are measured as the difference between final and initial cumulative gas volumes for the permeate and non-permeate ΔV (m^3) measured during time period Δt, i.e., $q = \Delta V/\Delta t$.[18] For air,

$$\text{Recovery of } O_2 = \frac{q_p C_{O_2,p}}{q_f C_{O_2,f}} \tag{15.41}$$

$$\text{Recovery of } N_2 = \frac{q_r C_{N_2,r}}{q_f C_{N_2,f}} \tag{15.42}$$

The term "stage cut" is used to define the ratio of permeate flow rate to total flow rate as shown in Equation (15.43). The concentrations and volumetric flow rates are usually measured at atmospheric pressure for both the permeate and the non-permeate streams. If this were not the case, stage cut would be defined as the ratio of molar flows instead of volumetric flows[18]

$$\text{Stage cut} = \frac{q_p}{q_p + q_r} \tag{15.43}$$

The total flux of a component, J_i, may be calculated from Equation (15.44)

$$J_i = \frac{q_{ip}\rho}{nA} \tag{15.44}$$

where q_{ip} = volumetric flow rate of species i in the permeate (m^3/s)
ρ = density of permeate ($gmol/m^3$)
A = area of membrane (m^2/module)
n = number of modules used

If values of the aforementioned terms P_i and t cannot be determined independently from experiment or the literature, an intrinsic permeability P_i^* is used where P_i^* has units of $lb/ft^2 \cdot h \cdot psi$:

$$P_i^* = \frac{P_i}{t_m} = \frac{J_i}{p_{i2} - p_{i1}} \tag{15.45}$$

Note that permeate pressure is assumed to be atmospheric (0 psig) in these equations. The operating pressure should be expressed as a pressure differential (usually psi), although some references use absolute pressure on the feed side of the membrane.[22]

ILLUSTRATIVE EXAMPLE 15.15

Figure 15.9 shows a block flow diagram representing mass balances for a gas permeation system which was provided by a recent Manhattan College chemical engineering student. Note that the feed stream is air and the two product streams are a non-permeate nitrogen-enriched stream and a permeate oxygen-enriched stream). Comment on Figure 15.9.

***SOLUTION*:** As noted below, the mass balances are satisfied.

Overall:

$$F_F = F_{NP} + F_P$$
$$0.104 = 0.0932 + 0.011$$
$$= 0.1042$$

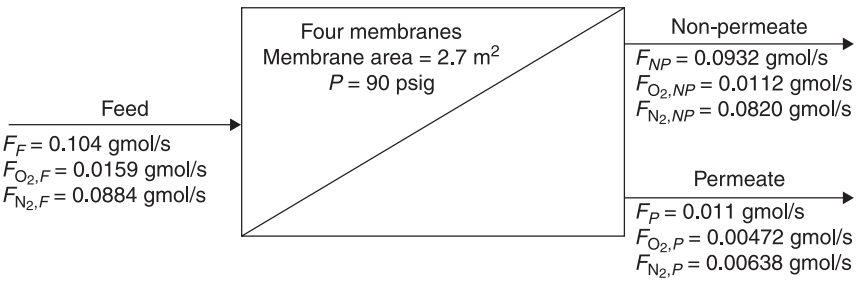

Figure 15.9 Gas permeation flow diagram.

Componential O_2:

$$\begin{aligned} F_{O_2,F} &= F_{O_2,NP} + F_{O_2,P} \\ 0.0159 &= 0.0112 + 0.00472 \\ &= 0.01592 \end{aligned}$$

Componential N_2:

$$\begin{aligned} F_{N_2,F} &= F_{N_2,NP} + F_{N_2,P} \\ 0.0884 &= 0.0820 + 0.00638 \\ &= 0.08838 \end{aligned}$$

However, the oxygen mole fraction in the air feed is

$$y_{O_2} = \frac{0.0159}{0.104} = 0.153 = 15.3\%$$

and the nitrogen in the feed is

$$y_{N_2} = 1 - y_{O_2} = 0.847 = 84.7\%$$

This does *not* compare favorably with the 21%/79% makeup normally assumed for air. ■

ILLUSTRATIVE EXAMPLE 15.16

Refer to the previous example. Calculate the percentage nitrogen recovery in the non-permeate.

***SOLUTION*:** The percentage recovery of nitrogen in the non-permeate stream can be calculated using Equation (15.42). Since the molar flow rates are specified in Figure 15.9, the N_2 recovery is given by

$$\begin{aligned} \%\,\text{Recovery } N_2 &= \left(\frac{F_{N_2,NP}}{F_{N_2,F}}\right)100;\ F = \text{qC} \\ &= \left(\frac{0.0820}{0.0884}\right)100 \\ &= 92.8\% = 0.928 \end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 15.17

Refer to Illustrative Example 15.16. Calculate the percent oxygen recovery in the permeate.

***SOLUTION*:** The percentage recovery of oxygen in the permeate stream is also calculated using Equation (15.42).

$$\begin{aligned} \%\ \text{Recovery } O_2 &= \left(\frac{F_{O_2,P}}{F_{O_2,F}}\right)100 \\ &= \left(\frac{0.00472}{0.0159}\right)100 \\ &= 29.7\% = 0.297 \end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 15.18

Refer to Illustrative Example 15.5. Calculate the separation factor based on the permeate and on the feed.

***SOLUTION*:** The separation factor, based on the permeate stream, is calculated using Equation (15.39). From Figure 15.9,

$$y_{O_2,P} = \frac{0.00472}{0.011} = 0.429 = 0.43$$

$$y_{O_2,NP} = \frac{0.0112}{0.0932} = 0.012$$

Substituting

$$a'_{O_2,N_2} = \frac{y_{O_2,P}/y_{N_2,P}}{y_{O_2,NP}/y_{N_2,NP}} = \frac{0.43/(1-0.43)}{0.12/(1-0.12)} = 5.5322$$

The separation factor based on the feed stream is calculated using Equation (15.40). For this case

$$y_{O_2,F} = \frac{0.0159}{0.104} = 0.1528 = 0.15$$

Therefore

$$a''_{O_2,N_2} = \frac{y_{O_2,P}/y_{N_2,P}}{y_{O_2,f}/y_{N_2,f}} = \frac{0.43/(1-0.43)}{0.15/(1-0.15)} = 4.27$$

■

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