MEMBRANE TECHNOLOGY

1. Introduction

Membranes have gained an important place in chemical technology and are being used increasingly in a broad range of applications. The key property that is exploited in every application is the ability of a membrane to control the permeation of a chemical species in contact with it. In packaging applications, the goal is usually to prevent permeation completely. In controlled drug delivery applications, the goal is to moderate the permeation rate of a drug from a reservoir to the body. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components. Since the 1960s, membrane science has grown from a laboratory curiosity to a widely practiced technology in industry and medicine. This growth is likely to continue for some time, particularly in the membrane gas separation and pervaporation separation areas. Membranes will play a critical role in the next generation of biomedical devices, such as the artificial pancreas and liver. The total membrane market grew from $10 million to the $2–3 billion level in the 40 years prior to 2000. Spectacular growth of this magnitude is unlikely to continue, but a doubling in the size of the total industry to the $5 billion level during the decade following is likely.

2. Historical Development

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher scientists. For example, Abbé Nolet coined the word osmosis to describe permeation of water through a diaphragm in 1748. Through the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses but were used as laboratory tools to develop physical/chemical theories.

For example, the measurements of solution osmotic pressure made with membranes by Traube and Pfeffer were used by van't Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute solutions. This work led directly to the van't Hoff equation. At about the same time, the concept of a perfectly selective semipermeable membrane was used by Maxwell and others in developing the kinetic theory of gases.

Early investigators experimented with any type of diaphragm available to them, such as bladders of pigs, cattle, or fish, and sausage casings made of animal gut. Later, collodion (nitrocellulose) membranes were preferred, because they could be made reproducibly. In 1907, Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test (1). Other workers (2–4) improved on Bechhold's technique, and by the early 1930s microporous collodion membranes were commercially available. During the next 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate. Membranes found their first significant application in the filtration of drinking water samples at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down, and filters to test for water safety were needed urgently. The research effort to develop these filters, sponsored by the U.S. Army, was later exploited by the Millipore Corporation, the first and still the largest microfiltration membrane producer.

By 1960, the elements of modern membrane science had been developed, but membranes were used in only a few laboratory and small, specialized industrial applications. No significant membrane industry existed, and total annual sales of membranes for all applications probably did not exceed $10 million in 2000 dollars. Membranes suffered from four problems that prohibited their widespread use as a separation process: they were too unreliable, too slow, too unselective, and too expensive. Partial solutions to each of these problems have been developed since the 1960s, and now membrane-based separation processes are commonplace.

The seminal discovery that transformed membrane separation from a laboratory to an industrial process was the development, in the early 1960s, of the Loeb-Sourirajan process for making defect-free, high flux, asymmetric reverse osmosis membranes (5). These membranes consist of an ultrathin, selective surface film on a microporous support, which provides the mechanical strength. The flux of the first Loeb-Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis practical. The work of Loeb and Sourirajan, and the timely infusion of large sums of research dollars from the U.S. Department of Interior, Office of Saline Water (OSW), resulted in the commercialization of reverse osmosis (qv) and was a primary factor in the development of ultrafiltration (qv) and microfiltration. The development of electrodialysis was also aided by OSW funding.

The 20-year period from 1960 to 1980 produced a significant change in the status of membrane technology. Building on the original Loeb-Sourirajan membrane technology, other processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high performance membranes. Using these processes, membranes with selective layers as thin as 0.1 μm or less can be made. Methods of packaging membranes into spiral-wound, hollow-fine fiber, capillary, and plate-and-frame modules were also developed, and advances were made in improving membrane stability. By 1980, microfiltration, ultrafiltration, reverse osmosis, and electrodialysis were all established processes with large plants installed around the world.

The principal development in the 1980s was the emergence of industrial membrane gas-separation processes. The first significant development was the Monsanto Prism membrane for hydrogen separation, developed in the late 1970s (6). Within a few years, Dow was producing systems to separate nitrogen from air, and Cynara and Separex were producing systems to separate carbon dioxide from methane. Gas-separation technology is evolving and expanding rapidly, and further substantial growth will be seen in the 1990s. The final development of the 1980s was the introduction by GFT, a small German engineering company, of the first commercial pervaporation systems for dehydration of alcohol. By 1990, GFT had sold more than 100 plants. Many of these plants are small, but the technology has been demonstrated and a number of other pervaporation applications are at the pilot-plant stage.

3. Types of Membrane

Although this article is limited to synthetic membranes, excluding all biological structures, the topic is still large enough to include a wide variety of membranes that differ in chemical and physical composition and in the way they operate. In essence, a membrane is a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example, containing holes or pores of finite dimensions. A normal filter meets this definition of a membrane, but, by convention, the term membrane is usually limited to structures that permeate dissolved or colloidal species, whereas the term filter is used to designate structures that separate particulate suspensions. The principal types of membrane are shown schematically in Figure 1.

3.1. Isotropic Microporous Membranes. A microporous membrane is very similar in its structure and function to a conventional filter. It has a rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, of the order of 0.01–10 μm in diameter. All particles larger than the largest pores are completely rejected by the membrane. Particles smaller than the largest pores, but larger than the smallest pores are partially rejected, according to the pore size distribution of the membrane. Particles much smaller than the smallest pores pass through the membrane. Thus separation of solutes by microporous membranes is mainly a function of molecular size and pore size distribution. In general, only molecules that differ considerably in size can be separated effectively by microporous membranes, for example, in ultrafiltration and microfiltration.

3.2. Nonporous Dense Membranes. Nonporous, dense membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a solution is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. An important property of nonporous, dense membranes is that even permeants of similar size may be separated when their concentration in the membrane material (ie, their solubility) differs significantly. Most gas separation, pervaporation, and reverse osmosis membranes use dense membranes to perform the separation. However, these membranes usually have an asymmetric structure to improve the flux.

3.3. Electrically Charged Membranes. Electrically charged membranes can be dense or microporous, but are most commonly microporous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing negatively charged ions is called a cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. The separation is affected by the charge and concentration of the ions in solution. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis.

3.4. Asymmetric Membranes. The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong, defect-free films to about 20 μm thickness. The development of novel membrane fabrication techniques to produce asymmetric membrane structures was one of the breakthroughs of membrane technology during the past 30 years. Asymmetric membranes consist of an extremely thin surface layer supported on a much thicker porous, dense substructure. The surface layer and its substructure may be formed in a single operation or formed separately. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by asymmetric membranes are so great that almost all commercial processes use such membranes.

3.5. Ceramic, Metal, and Liquid Membranes. The discussion so far implies that membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer based. However, interest in membranes formed from less conventional materials has increased. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration applications, for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from gas mixtures, and supported or emulsified liquid films are being developed for coupled and facilitated transport processes.

4. Preparation of Membranes and Membrane Modules

Because membranes applicable to diverse separation problems are often made by the same general techniques, classification by end use application or preparation method is difficult. The first part of this section is, therefore, organized by membrane structure; preparation methods are described for symmetrical membranes, asymmetric membranes, ceramic and metal membranes, and liquid membranes. The production of hollow-fine fiber membranes and membrane modules is then covered. Symmetrical membranes have a uniform structure throughout; such membranes can be either dense films or microporous.

4.1. Dense Symmetrical Membranes. These membranes are used on a large scale in packaging applications (see FILM AND SHEETING MATERIALS; PACKAGING, CONTAINERS FOR INDUSTRIAL MATERIALS). They are also used widely in the laboratory to characterize membrane separation properties. However, it is difficult to make mechanically strong and defect-free symmetrical membranes thinner than 20 μm, so the flux is low, and these membranes are rarely used in separation processes.

For laboratory work, the membranes are prepared by solution casting or by melt pressing.

In solution casting, a casting knife or drawdown bar is used to spread an even film of an appropriate polymer solution across a glass plate. The casting knife consists of a steel blade, resting on two runners, arranged to form a precise gap between the blade and the plate on which the film is cast. A typical hand-casting knife is shown in Figure 2. After the casting has been made, it is left to stand, and the solvent evaporates to leave a uniform polymer film.

The polymer casting solution should be sufficiently viscous to prevent the solution from running over the casting plate, so typical casting solution concentrations are in the range of 15 to 20 wt% polymer. Solvents with high boiling points are inappropriate for solvent casting, because their low volatility demands long evaporation times. During an extended evaporation period, the cast film can absorb sufficient atmospheric water to precipitate the polymer, producing a mottled, hazy surface.

Many polymers, including polyethylene, polypropylene, and nylons, do not dissolve in suitable casting solvents. In the laboratory, membranes can be made from such polymers by melt pressing, in which the polymer is sandwiched at high pressure between two heated plates. A pressure of 13.8–34.5 MPa (2000–5000 psi) is applied for 0.5 to 5 minutes, at a plate temperature just above the melting point of the polymer. Melt forming is commonly used to make dense films for packaging applications, either by extrusion as a sheet from a die or as blown film.

4.2. Microporous Symmetrical Membranes. These membranes, used widely in microfiltration, typically contain pores in the range of 0.1–10 μm diameter. As shown in Figure 3, microporous membranes are generally characterized by the average pore diameter, d, the membrane porosity, ϵ (the fraction of the total membrane volume that is porous), and the tortuosity of the membrane, τ (a term reflecting the length of the average pore through the membrane compared to the membrane thickness). The most important types of microporous membrane are those formed by one of the solution–precipitation techniques discussed in the next section under asymmetric membranes; about half of all microporous membranes are made in this way. The remainder is made by various proprietary techniques, the more important of which are discussed in the following.

Irradiation. Nucleation track membranes were first developed by the Nuclepore Corporation (7). The two-step preparation process is illustrated in Figure 4. A polymer film is first irradiated with charged particles from a nuclear reactor or other radiation source; particles passing through the film break polymer chains and leave behind sensitized or damaged tracks. The film is then passed through an etch solution, which etches the polymer preferentially along the sensitized nucleation tracks, thereby forming pores. The length of time the film is exposed to radiation in the reactor determines the number of pores in the film; the etch time determines the pore diameter. Because of the unique preparation techniques used to make nucleation track membranes, the pores are uniform cylinders traversing the membrane almost at right angles. The membrane tortuosity is, therefore, close to 1.0. The membrane porosity is usually relatively low, about 5%, so fluxes are low. However, because these membranes are very close to a perfect screen filter, they are used in analytical techniques that require filtration of all particles above a certain size from a fluid so that the particles can be visualized under a microscope.

Expanded Film. Expanded-film membranes are made from crystalline polymers by an orientation and stretching process. In the first step of the process, a highly oriented film is produced by extruding the polymer at close to its melting point coupled with a very rapid drawdown (9,10). After cooling, the film is stretched a second time, up to 300%, at right angles to the original orientation of the polymer crystallites. This second elongation deforms the crystalline structure of the film and produces slit-like voids 20 to 250 nm wide between crystallites. The process is illustrated in Figure 5. This type of membrane was first developed by Hoechst-Celanese and is sold under the trade name Celgard; a number of companies make similar products. The membranes made by W. L. Gore, sold under the trade name Gore-Tex, are made by this type of process (11).

The original expanded film membranes were sold in rolls as flat sheets. These membranes had relatively poor tear strength along the original direction of orientation and were not widely used as microfiltration membranes. They did, however, find use as porous inert separating barriers in batteries and some medical devices. More recently, the technology has been developed to produce these membranes as hollow fibers, which are used as membrane contactors (12,13).

Template Leaching. Template leaching offers an alternative manufacturing technique for insoluble polymers. A homogeneous film is prepared from a mixture of the membrane matrix material and a leachable component. After the film has been formed, the leachable component is removed with a suitable solvent and a microporous membrane is formed (14,15). The leachable component could be a soluble low molecular weight solid or liquid, or even a polymeric material such as poly(vinyl alcohol) or poly(ethylene glycol). The same general method is used to prepare microporous glass (16). In this case, a two-component glass melt is formed into sheets or small tubes, after which one of the components is leached out by extraction with an alkaline solution.

4.3. Asymmetric Membranes. In industrial applications other than microfiltration, symmetrical membranes have been displaced almost completely by asymmetric membranes, which have much higher fluxes. Asymmetric membranes have a thin, permselective layer supported on a more open porous substrate. Hindsight makes it clear that many of the membranes produced in the 1930s and 1940s were asymmetric, although this was not realized at the time. The importance of the asymmetric structure was not recognized until Loeb and Sourirajan prepared the first high flux, asymmetric, reverse osmosis membranes by what is now known as the Loeb-Sourirajan technique (5). This discovery was a critical breakthrough in membrane technology. The reverse osmosis membranes produced were an order of magnitude more permeable than any symmetrical membrane produced previously. More importantly, demonstration of the benefits of the asymmetric structure paved the way for the development of other types of asymmetric membranes.

Phase Inversion (Solution Precipitation). Phase inversion, also known as solution precipitation or polymer precipitation, is the most important asymmetric membrane preparation method. In this process, a clear polymer solution is precipitated into two phases: a solid polymer-rich phase that forms the matrix of the membrane, and a liquid polymer-poor phase that forms the membrane pores. If precipitation is rapid, the pore-forming liquid droplets tend to be small and the membranes formed are markedly asymmetric. If precipitation is slow, the pore-forming liquid droplets tend to agglomerate while the casting solution is still fluid, so that the final pores are relatively large and the membrane structure is more symmetrical. Polymer precipitation from a solution can be achieved in several ways, such as cooling, solvent evaporation, precipitation by immersion in water, or imbibition of water from the vapor phase. Each technique was developed independently; only since the 1980s has it become clear that these processes can all be described by the same general approach based on polymer–solvent–nonsolvent phase diagrams. Thus, the Loeb-Sourirajan process, in which precipitation is produced by immersion in water, is a subcategory of the general class of phase-inversion membranes. The theory behind the preparation of membranes by all of these techniques has been reviewed in a number of monographs and review articles (17–20).

Polymer Precipitation by Cooling. The simplest solution–precipitation technique is thermal gelation, in which a film is cast from a hot, one-phase polymer solution. When the cast film cools, the polymer precipitates, and the solution separates into a polymer-matrix phase containing dispersed pores filled with solvent. The precipitation process that forms the membrane can be represented by the phase diagram shown in Figure 6. The pore volume in the final membrane is determined mainly by the initial composition of the cast film, because this determines the ratio of the polymer to liquid phase in the cooled film. However, the spatial distribution and size of the pores is determined largely by the rate of cooling and, hence, precipitation, of the film. In general, rapid cooling produces membranes with small pores (21,22).

Polymer precipitation by cooling to produce microporous membranes was first commercialized on a large scale by Akzo (23). Akzo markets microporous polypropylene and poly(vinylidine fluoride) membranes produced by this technique under the trade name Accurel. Polypropylene membranes are prepared from a solution of polypropylene in *N*,*N*-bis(2-hydroxyethyl)tallowamine. The amine and polypropylene form a clear solution at temperatures above 100–150°C. Upon cooling, the solvent and polymer phases separate to form a microporous structure. If the solution is cooled slowly, an open cell structure results. The interconnecting passageways between cells are generally in the micrometer range. If the solution is cooled and precipitated rapidly, a much finer structure is formed. The rate of cooling is, therefore, a key parameter determining the final structure of the membrane (21).

A schematic diagram of the polymer precipitation process is shown in Figure 7. The hot polymer solution is cast onto a water-cooled chill roll, which cools the solution, causing the polymer to precipitate. The precipitated film is passed through an extraction tank containing methanol, ethanol or 2-propanol to remove the solvent. Finally, the membrane is dried, sent to a laser inspection station, trimmed, and rolled up. The process shown in Figure 7 is used to make flat-sheet membranes. The preparation of hollow-fiber membranes (qv) by the same general technique has also been described.

Polymer Precipitation by Solvent Evaporation. This technique was one of the earliest methods of making microporous membranes (1–4). In the simplest form of the method, a polymer is dissolved in a two-component solvent mixture consisting of a volatile solvent, such as acetone, in which the polymer is readily soluble, and a less volatile nonsolvent, typically water or an alcohol. The polymer solution is cast onto a glass plate. As the volatile solvent evaporates, the casting solution is enriched in the nonvolatile solvent. The polymer precipitates, forming the membrane structure. The process can be continued until the membrane has completely formed, or it can be stopped, and the membrane structure fixed, by immersing the cast film into a precipitation bath of water or other nonsolvent. Scanning electron micrographs of some membranes made by this process are shown in Figure 8 (24).

Many factors determine the porosity and pore size of membranes formed by the solvent evaporation method. As Figure 8 shows, if the membrane is immersed in a nonsolvent after a short evaporation time, the resulting membrane will be finely microporous. If the evaporation step is prolonged before fixing the structure by immersion in water, the average pore size will be larger. In general, increasing the nonsolvent content of the casting solution, or decreasing the polymer concentration, increases porosity. It is important that the nonsolvent be completely incompatible with the polymer. If partly compatible nonsolvents are used, the precipitating polymer phase contains sufficient residual solvent to allow it to flow and collapse as the solvent evaporates. The result is a dense rather than microporous film.

Polymer Precipitation by Imbibition of Water Vapor. Preparation of microporous membranes by simple solvent evaporation alone is not practiced widely. However, a combination of solvent evaporation with precipitation by imbibition of water vapor from a humid atmosphere or by water-vapor imbibition in combination with solvent evaporation are the basis of many commercial phase-inversion processes. The processes often involve proprietary casting formulations that are not normally disclosed by membrane developers. However, during the development of composite membranes at Gulf General Atomic, this type of membrane was prepared and the technology described in some detail in a series of Office of Saline Water Reports (25). These reports remain the best published description of the technique. The casting solution typically consists of a blend of cellulose acetate and cellulose nitrate dissolved in a mixture of volatile solvents, such as acetone, and nonvolatile nonsolvents, such as water, ethanol, or ethylene glycol. The polymer solution is cast onto a continuous stainless steel belt. The cast film then passes through a series of environmental chambers; hot, humid air is usually circulated through the first chamber. The film loses the volatile solvent by evaporation and simultaneously absorbs water from the atmosphere. The total precipitation process is slow, taking about 10 minutes to complete. The resulting membrane structure is fairly symmetrical. After precipitation, the membrane passes to a second oven, through which hot dry air is circulated to evaporate the remaining solvent and dry the film. The formed membrane is then wound on a take-up roll. Typical casting speeds are of the order of 0.3–0.6 m/min. This type of membrane is widely used in microfiltration applications.

Polymer Precipitation by Immersion in a Nonsolvent Bath. This is the Loeb-Sourirajan process, the single most important membrane preparation technique, and almost all reverse osmosis, ultrafiltration, and many gas separation membranes are produced by this procedure or a derivative of it. A schematic of a casting machine used in the process is shown in Figure 9. A typical membrane casting solution contains approximately 20 wt% of dissolved polymer. This solution is cast onto a moving drum or paper web, and the cast film is precipitated by immersion in a water bath. The water precipitates the top surface of the cast film rapidly, forming an extremely dense, permselective skin. This skin slows down the entry of water into the underlying polymer solution, which precipitates much more slowly, forming a more porous substructure. Depending on the polymer, the casting solution and other parameters, the dense skin varies from 0.1 to 1.0 μm thick. This process was originally developed for reverse osmosis (5). Later the technique was adapted to make membranes for other applications, including ultrafiltration and gas separation (6,20,26).

A great deal of work has been devoted to rationalizing the factors affecting the properties of asymmetric membrane made by the Loeb-Sourirajan technique and, in particular, to understanding those factors that determine the thickness of the membrane skin that performs the separation. The goal is to make this skin as thin as possible, but still defect-free. The skin layer can be dense, as in reverse osmosis or gas separation, or finely microporous with pores in the 10–50 nm diameter range, as in ultrafiltration. In good quality membranes made by this technique, a skin thickness as low as 50–100 nm can be achieved. A scanning electron micrograph of a Loeb-Sourirajan membrane is shown in Figure 10.

The phase-diagram approach has been widely used to rationalize the preparation of these membranes (17–20,26). The ternary phase diagram of the three-component system used in preparing Loeb-Sourirajan membranes is shown in Figure 11. The corners of the triangle represent the three components, polymer, solvent, and precipitant; any point within the triangle represents a mixture of three components. The system consists of two regions: a one-phase region, where all components are miscible, and a two-phase region, where the system separates into a solid (polymer-rich) phase and a liquid (polymer-poor) phase. Although the one-phase region in the phase diagram is thermodynamically continuous, for practical purposes it can conveniently be divided into a liquid and solid gel region. Thus, at low polymer concentrations, the system is a low viscosity liquid, but as the concentration of polymer is increased, the viscosity of the system also increases rapidly, reaching such high values that the system can be regarded as a solid. The transition between liquid and solid regions is, therefore, arbitrary, but can be placed at a polymer concentration of 30–40 wt%. In the two-phase region of the diagram, tie lines link the polymer-rich and polymer-poor phases. Unlike low molecular weight components, polymer systems in the two-phase region are often slow to separate into different phases and metastable states are common, especially when a polymer solution is rapidly precipitated.

The phase diagram in Figure 11 shows the precipitation pathway of the casting solution during membrane formation. During membrane formation, the system changes from a composition A, which represents the initial casting solution composition, to a composition D, which represents the final membrane composition. At composition D, the two phases are in equilibrium: a solid (polymer-rich) phase, which forms the final membrane structure, represented by point S, and a liquid (polymer-poor) phase, which constitutes the membrane pores filled with precipitant, represented by point L. The position D on the line S–L determines the overall porosity of the membrane. The entire precipitation process is represented by the path A–D, during which the solvent is exchanged by the precipitant. The point B along the path is the concentration at which the first polymer precipitates. As precipitation proceeds, more solvent is lost and precipitant is imbibed by the polymer-rich phase, so the viscosity rises. At some point, the viscosity is high enough for the precipitated polymer to be regarded as a solid. This composition is at C in Figure 11. Once the precipitated polymer solidifies, further bulk movement of the polymer is hindered. The rate and the pathway A–D taken by the polymer solution vary from the surface of the polymer film to the sublayer, affecting the pore size and porosity of the final membrane at that point. The nature of the casting solution and the precipitation conditions are important in determining the kinetics of this precipitation process, and detailed theoretical treatments based on the ternary phase diagram approach have been worked out.

In the Loeb-Sourirajan process formation of minute membrane defects may occur. These defects, caused by gas bubbles, dust particles, and support fabric imperfections, are often difficult to eliminate. These defects may not significantly affect the performance of asymmetric membranes used in liquid separation operations, such as ultrafiltration and reverse osmosis, but can be disastrous in gas separation applications. Membrane defects can be overcome by coating the membrane with a thin layer of relatively permeable material (6,27). If the coating is sufficiently thin, it does not change the properties of the underlying permselective layer, but it does plug membrane defects, preventing simple convective gas flow through defects. This concept has been used to seal defects in polysulfone Loeb-Sourirajan membranes with silicone rubber (6). The form of these membranes is shown in Figure 12. The silicone rubber layer does not function as a selective barrier but rather plugs up defects, thereby reducing nondiffusive gas flow. The flow of gas through the portion of the silicone rubber layer over the pore is very high compared to the flow through the defect-free portion of the membrane. However, because the total area of the membrane subject to defects is very small, the total gas flow through these plugged defects is negligible. When this coating technique is used, the polysulfone skin layer of the Loeb-Sourirajan membrane no longer has to be completely free of defects; the coated membrane can be made with a thinner skin than is possible with an uncoated membrane. The increase in flux brought about by decreasing the thickness of the permselective skin layer more than compensates for the slight reduction in flux due to the silicone rubber sealing layer.

Cellulose acetate Loeb-Sourirajan reverse osmosis membranes were introduced commercially in the 1960s. Since then, many other polymers have been made into asymmetric membranes in attempts to improve membrane properties. In the reverse osmosis area, these attempts have had limited success, the only significant example being Du Pont's polyamide membrane. For gas separation and ultrafiltration, a number of membranes with useful properties have been made. However, the early work on asymmetric membranes has spawned numerous other techniques in which a microporous membrane is used as a support to carry another thin, dense separating layer.

Interfacial Composite Membranes. A method of making asymmetric membranes involving interfacial polymerization was developed in the 1960s. This technique was used to produce reverse osmosis membranes with dramatically improved salt rejections and water fluxes compared to those prepared by the Loeb-Sourirajan process (28). In the interfacial polymerization method, an aqueous solution of a reactive prepolymer, such as polyamine, is first deposited in the pores of a microporous support membrane, typically a polysulfone ultrafiltration membrane. The amine-loaded support is then immersed in a water-immiscible solvent solution containing a reactant, for example, a diacid chloride in hexane. The amine and acid chloride then react at the interface of the two solutions to form a densely cross-linked, extremely thin membrane layer. This preparation method is shown schematically in Figure 13. The first membrane made was based on polyethylenimine cross-linked with toluene-2,4-diisocyanate (28). The process was later refined at FilmTec Corporation (29,30) and at UOP (31) in the United States, and at Nitto (32) in Japan.

Membranes made by interfacial polymerization have a dense, highly cross-linked interfacial polymer layer formed on the surface of the support membrane at the interface of the two solutions. A less cross-linked, more permeable hydrogel layer forms under this surface layer and fills the pores of the support membrane. Because the dense cross-linked polymer layer can only form at the interface, it is extremely thin, on the order of 0.1 μm or less, and the permeation flux is high. Because the polymer is highly cross-linked, its selectivity is also high. The first reverse osmosis membranes made this way were 5–10 times less salt-permeable than the best membranes with comparable water fluxes made by other techniques.

Interfacial polymerization membranes are less applicable to gas separation because of the water swollen hydrogel that fills the pores of the support membrane. In reverse osmosis, this layer is highly water swollen and offers little resistance to water flow, but when the membrane is dried and used in gas separations the gel becomes a rigid glass with very low gas permeability. This glassy polymer fills the membrane pores and, as a result, defect-free interfacial composite membranes usually have low gas fluxes, although their selectivities can be good.

Solution-Cast Composite Membranes. Another important type of composite membrane is formed by solution casting a thin (0.5–2.0 μm) film on a suitable microporous film. Membranes of this type were first prepared at General Electric (27,33) and at North Star Research (34) using a type of Langmuir trough system (33,34). In this system, a dilute polymer solution in a volatile water-insoluble solvent is spread over the surface of a water-filled trough. The thin polymer film formed on the water surface is then picked up on a microporous support. This technique was developed into a semicontinuous process at General Electric but has not proved reliable enough for large-scale commercial use.

Most solution-cast composite membranes are prepared by a technique pioneered at UOP (35). In this technique, a polymer solution is cast directly onto the microporous support film. The support film must be clean, defect-free, and very finely microporous, to prevent penetration of the coating solution into the pores. If these conditions are met, the support can be coated with a liquid layer 50–100 μm thick, which after evaporation leaves a thin permselective film, 0.5–2 μm thick.

This technique was used to form the Monsanto Prism gas separation membranes (6) and at Membrane Technology and Research to form pervaporation and organic vapor–air separation membranes (36,37).

Other Asymmetric Membrane Preparation Techniques. A number of other methods of preparing membranes have been reported in the literature and are used on a small scale. Table 1 provides a brief summary of these techniques.

4.4. Metal and Ceramic Membranes. Palladium and palladium alloy membranes can be used to separate hydrogen from other gases. Palladium membranes were studied extensively during the 1950s and 1960s, and a commercial plant to separate hydrogen from refinery off-gas was installed by Union Carbide (53). The plant used palladium–silver alloy membranes in the form of 25-μm thick films. The plant was operated for some time, but a number of problems, including long-term membrane stability under the high temperature operating conditions, were encountered, and the plant was later replaced by pressure-swing adsorption systems. Small-scale palladium membrane systems, marketed by Johnson Matthey and Co., are still used to produce ultrapure hydrogen for specialized applications. These systems use palladium–silver alloy membranes, based on those originally developed (54). Membranes with much thinner effective palladium layers than were used in the Union Carbide installation can now be made. One technique is to form a composite membrane comprising a polymer substrate onto which is coated a thin layer of palladium or palladium alloy (55). The palladium layer can be applied by vacuum methods, such as evaporation or sputtering. Coating thicknesses on the order of 100 nm or less can be achieved.

Ceramic Membranes. A number of companies have developed ceramic membranes for ultrafiltration and microfiltration applications. Ceramic membranes have the advantages of being extremely chemically inert and stable at high temperatures, conditions under which polymer films fail. Ceramic membranes can be made by three processes: sintering, leaching, and sol–gel techniques. Sintering involves taking a colloidal suspension of particles, forming a coagulated thin film, and then heat treating the film to form a continuous, porous structure. The pore sizes of sintered films are relatively large, on the order of 10–100 μm. In the leaching process, a glass sheet or capillary incorporating two intermixed phases is treated with an acid or alkali that dissolves one of the phases. Smaller pores can be obtained by this method, but the uniformity of the structure is difficult to control. The preparation of ceramic membranes by sol–gel techniques is the newest approach, and offers the greatest potential for making finely porous membranes.

Figure 14 summarizes the available sol–gel processes (56). The process on the right of the figure involves the hydrolysis of metal alkoxides in a water–alcohol solution. The hydrolyzed alkoxides are polymerized to form a chemical gel, which is dried and heat treated to form a rigid oxide network held together by chemical bonds. This process is difficult to carry out, because the hydrolysis and polymerization must be carefully controlled. If the hydrolysis reaction proceeds too far, precipitation of hydrous metal oxides from the solution starts to occur, causing agglomerations of particulates in the sol.

In the process in the center of Figure 14, complete hydrolysis is allowed to occur. Bases or acids are added to break up the precipitate into small particles. Various reactions based on electrostatic interactions at the surface of the particles take place: the result is a colloidal solution. Organic binders are added to the solution and a physical gel is formed. The gel is then heat treated as before to form the ceramic membrane.

The sol–gel technique has been used mostly to prepare alumina membranes. Figure 15 shows a cross section of a composite alumina membrane made by slip coating successive sols with different particle sizes onto a porous ceramic support. Silica or titanium membranes could also be made by the same principles. Unsupported titanium dioxide membranes with pore sizes of 5 nm or less have been made by the sol–gel process (57).

4.5. Liquid Membranes. A number of reviews summarize the considerable research effort in the 1970s and 1980s on liquid membranes containing carriers to facilitate selective transport of gases or ions (58,59). Although still being explored in a number of laboratories, the more recent development of much more selective conventional polymer membranes has diminished interest in processes using liquid membranes.

4.6. Hollow-Fiber Membranes. Most of the techniques described in the foregoing were developed originally to produce flat-sheet membranes, but the majority can be adapted to produce membranes in the form of thin tubes or fibers. Formation of membranes into hollow fibers has a number of advantages, one of the most important of which is the ability to form compact modules with very high surface areas. This advantage is offset, however, by the generally lower fluxes of hollow-fiber membranes compared to flat-sheet membranes made from the same materials. Nonetheless, the development of hollow-fiber membranes at Dow Chemical in 1966 (60), and their later commercialization by Dow, Monsanto, Du Pont, and others represents one of the most significant events in membrane technology (see MEMBRANES, HOLLOW-FIBER).

Hollow fibers are usually on the order of 25 μm to 2 mm in diameter. They can be made with a homogeneous dense structure, or preferably with a microporous structure having a dense permselective layer on the outside or inside surface. The dense surface layer can be integral, or separately coated onto a support fiber. The fibers are packed into bundles and potted into tubes to form a membrane module. More than a kilometer of fibers may be required to form a membrane module with a surface area of one square meter. A module can have no breaks or defects, requiring very high reproducibility and stringent quality control standards. Fibers with diameters 25 to 200 μm are usually called hollow-fine fibers. The feed fluid is generally applied to the outside of the fibers and the permeate removed down the bore. Fibers with diameters in the 200 μm to 2 mm range are called capillary fibers. The feed fluid is commonly applied to the inside bore of the fiber, and the permeate is removed from the outer shell.

Hollow-fiber fabrication methods can be divided into two classes (61). The most common is solution spinning, in which a 20–30% polymer solution is extruded and precipitated into a bath of a nonsolvent, generally water. Solution spinning allows fibers with the asymmetric Loeb-Sourirajan structure to be made. An alternative technique is melt spinning, in which a hot polymer melt is extruded from an appropriate die and is then cooled and solidified in air or a quench tank. Melt-spun fibers are usually relatively dense and have lower fluxes than solution-spun fibers, but because the fiber can be stretched after it leaves the die, very fine fibers can be made. Melt spinning can also be used with polymers such as poly(trimethylpentene), which are not soluble in convenient solvents and are difficult to form by wet spinning.

Solution (Wet) Spinning. In the most widely used solution spinnerette system (60) the spinnerette consists of two concentric capillaries, the outer capillary having a diameter of approximately 400 μm and the central capillary having an outer diameter of approximately 200 μm and an inner diameter of 100 μm. Polymer solution is forced through the outer capillary while air or liquid is forced through the inner one. The rate at which the core fluid is injected into the fibers relative to the flow of polymer solution governs the ultimate wall thickness of the fiber. Figure 16 shows a cross section of this type of spinnerette.

A complete hollow-fiber spinning system is shown in Figure 17. Fibers are formed almost instantaneously as the polymer solution leaves the spinnerette. The amount of evaporation time between the solution exiting the spinnerette and entering the coagulation bath is a critical variable. If water is forced through the inner capillary, an asymmetric hollow fiber is formed with the skin on the inside. If air under pressure, or an inert liquid, is forced through the inner capillary to maintain the hollow core, the skin is formed on the outside of the fiber by immersion into a suitable coagulation bath (62).

Wet spinning of this type of hollow fiber is a well-developed technology, especially in the preparation of dialysis membranes for use in artificial kidneys. Systems that spin more than 100 fibers simultaneously on an around-the-clock basis are in operation. Wet-spun fibers are also used widely in ultrafiltration applications, in which the feed solution is forced down the bore of the fiber. Nitto, Asahi, Microgon, and Romicon all produce this type of fiber, generally with diameters of 1–3 mm.

Melt Spinning. In melt spinning, the polymer is extruded through the outer capillary of the spinnerette as a hot melt, the spinnerette assembly being maintained at a temperature between 100 and 300°C. The polymer can be extruded either as a pure melt or as a blended dope containing small amounts of plasticizers and other additives. Melt-spun fibers are usually stretched as they leave the spinnerette, to form very thin fibers. Formation of such small-diameter fibers is a significant advantage of melt spinning over solution spinning. The dense nature of melt-spun fibers leads to lower fluxes than can be obtained with solution-spun fibers, but because of the enormous membrane surface area of these fine hollow fibers, this may not be a problem.

4.7. Membrane Modules. A useful membrane process requires the development of a membrane module containing large surface areas of membrane. The development of the technology to produce low cost membrane modules was one of the breakthroughs that led to the commercialization of membrane processes in the 1960s and 1970s. The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press: these are called plate-and-frame modules. Systems containing a number of membrane tubes were developed at about the same time. Both of these systems are still used, but because of their relatively high cost they have been largely displaced by two other designs: the spiral-wound module and the hollow-fiber module.

Spiral-Wound Modules. Spiral-wound modules were used originally for artificial kidneys, but were fully developed for reverse osmosis systems. This work, carried out by UOP under sponsorship of the Office of Saline Water (later the Office of Water Research and Technology) resulted in a number of spiral-wound designs (63–65). The design shown in Figure 18 is the simplest and most common, and consists of a membrane envelope wound around a perforated central collection tube. The wound module is placed inside a tubular pressure vessel, and feed gas is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals toward the center and exits through the collection tube.

Small laboratory spiral-wound modules consist of a single membrane enveloped wrapped around the collection tube. The membrane area of these modules is typically 0.6−1.0 m^2. Commercial spiral-wound modules are typically 100−150 cm long and have diameters of 10, 15, 20, and 30 cm. These modules consist of a number of membrane envelopes, each with an area of approximately 2 m^2, wrapped around the central collection pipe. This type of multileaf design is illustrated in Figure 19 (64). Such designs are used to minimize the pressure drop encountered by the permeate fluid traveling toward the central pipe. If a single membrane envelope were used in these large-diameter modules, the path taken by the permeate to the central collection pipe would be 5−25 meters depending on the module diameter. This long permeate path would produce a very large pressure drop, especially with high flux membranes. If multiple, smaller envelopes are used in a single module, the pressure drop in any one envelope is reduced to a manageable level.

Hollow-Fiber Modules. Hollow-fiber membrane modules are formed in two basic geometries. The first is the shell-side feed design illustrated in Figure 20**a** and used, for example, by Monsanto in their hydrogen separation systems or by Du Pont in their reverse osmosis fiber systems. In such a module, a loop or a closed bundle of fiber is contained in a pressure vessel. The system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support a considerable hydrostatic pressure, these fibers are usually made by melt spinning and usually have a small diameter, on the order of 100 μm ID and 150−200 μm OD.

The second type of hollow-fiber module is the bore-side feed type illustrated in Figure 20**b**. The fibers in this type of unit are open at both ends, and the feed fluid is usually circulated through the bore of the fibers. To minimize pressure drops inside the fibers, the fibers often have larger diameters than the very fine fibers used in the shell-side feed system and are generally made by solution spinning. These so-called capillary fibers are used in ultrafiltration, pervaporation, and in some low to medium pressure gas applications. Feed pressures are usually limited to less than 1 MPa (150 psig) in this type of module.

Plate-and-Frame Modules. Plate-and-frame modules were among the earliest types of membrane system; the design originates from the conventional filter-press. Membrane, feed spacers, and product spacers are layered together between two end plates. A number of plate-and-frame units have been developed for small-scale applications, but these units are expensive compared to the alternatives, and leaks caused by the many gasket seals are a serious problem. Plate-and-frame modules are generally limited to electrodialysis and pervaporation systems and a limited number of highly fouling reverse osmosis and ultrafiltration applications.

Tubular Modules. Tubular modules are generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling because of good fluid hydrodynamics overcomes the problem of their high capital cost. Typically, the tubes consist of a porous paper or fiber glass support with the membrane formed on the inside of the tubes, as shown in Figure 21.

Module Selection. The choice of the appropriate membrane module for a particular membrane separation balances a number of factors. The principal factors that enter into this decision are listed in Table 2.

Cost, although always important, is difficult to quantify because the actual selling price of membrane modules varies widely, depending on the application. Generally, high pressure modules are more expensive than low pressure or vacuum systems. The selling price also depends on the volume of the application and the pricing structure adopted by the industry. For example, spiral-wound modules for reverse osmosis of brackish water are produced by many manufacturers, resulting in severe competition and low prices, whereas similar modules for use in gas separation are much more expensive. An estimate of module manufacturing cost is given in Table 2; the selling price is typically two to five times higher.

A second factor determining module selection is resistance to fouling. Membrane fouling is a particularly important problem in liquid separations such as reverse osmosis and ultrafiltration. In gas separation applications, fouling is more easily controlled. Hollow-fine fibers are notoriously prone to fouling and can only be used in reverse osmosis applications if extensive, costly feed-solution pretreatment is used to remove all particulates. These fibers cannot be used in ultrafiltration applications at all.

A third factor is the ease with which various membrane materials can be fabricated into a particular module design. Almost all membranes can be formed into plate-and-frame, spiral, and tubular modules, but many membrane materials cannot be fabricated into hollow-fine fibers or capillary fibers. Finally, the suitability of the module design for high pressure operation and the relative magnitude of pressure drops on the feed and permeate sides of the membrane can sometimes be important considerations.

In reverse osmosis, most modules are of the hollow-fine fiber or spiral-wound design; plate-and-frame and tubular modules are limited to a few applications in which membrane fouling is particularly severe, for example, food applications or processing of heavily contaminated industrial wastewater. Hollow-fiber designs are being displaced by spiral-wound modules, which are inherently more fouling resistant, and require less feed pretreatment. Also, thin-film interfacial composite membranes, the best reverse osmosis membranes available, have not been fabricated in the form of hollow-fine fibers.

For ultrafiltration applications, hollow-fine fibers have never been seriously considered because of their susceptibility to fouling. If the feed solution is extremely fouling, tubular or plate-and-frame systems are still used. Recently, however, spiral-wound modules with improved resistance to fouling have been developed, and these modules are increasingly displacing the more expensive plate-and-frame and tubular systems. Capillary systems are also used in some ultrafiltration applications.

For high pressure gas separation applications, hollow-fine fibers appear to have a large segment of the market. Hollow-fiber modules are clearly the lowest cost design per unit membrane area, and the poor resistance of hollow-fiber modules to fouling is not a problem in many gas-separation applications. Also, gas separation membrane materials are often rigid glassy polymers such as polysulfones, polycarbonates, and polyimides, which can be easily formed into hollow-fine fibers. Of the principal companies servicing this area only Separex and W. R. Grace use spiral-wound modules. Both companies use these modules to process natural gas streams, which are relatively dirty, often containing oil mist and condensable components that would foul hollow-fine fiber modules rapidly.

Spiral-wound modules are much more commonly used in low pressure or vacuum gas separation applications, such as the production of oxygen-enriched air, or the separation of organic vapors from air. In these applications, the feed gas is at close to ambient pressure, and a vacuum is drawn on the permeate side of the membrane. Parasitic pressure drops on the permeate side of the membrane and the difficulty in making high performance hollow-fine fiber membranes from the rubbery polymers used to make these membranes both work against hollow-fine fiber modules for this application.

Pervaporation operates under constraints similar to low pressure gas-separation. Pressure drops on the permeate side of the membrane must be small, and many prevaporation membrane materials are rubbery. For this reason, spiral-wound modules and plate-and-frame systems are both in use. Plate-and-frame systems are competitive in this application despite their high cost, primarily because they can be operated at high temperatures with relatively aggressive feed solutions, for which spiral-wound modules might fail.

5. Applications

The principal use of membranes in the chemical processing industry is in various separation processes. Seven major membrane separation processes are discussed in this section. These can be classified into technologies that are developed, developing, or to-be-developed, as shown in Table 3. Membranes, or rather films, are also used widely as packaging materials. The use of membranes in various biomedical applications, for example, in controlled release technology and in artificial organs such as the artificial kidney, lung, and pancreas are only covered briefly here.

The four developed processes are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. All are well established, and the market is served by a number of experienced companies. The first three processes are related to filtration techniques, in which a solution containing dissolved or suspended solids is forced through a membrane filter. The solvent passes through the membrane; the solutes are retained. The three processes differ principally in the size of the particles separated by the membrane. Microfiltration is considered to refer to membranes with pore diameters from 0.1 μm (100 nm) to 10 μm. Microfiltration membranes are used to filter suspended particulates, bacteria, or large colloids from solutions. Ultrafiltration refers to membranes having pore diameters in the range 2–100 nm. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solution. Typical applications of ultrafiltration membranes are concentrating proteins from milk whey, or recovering colloidal paint particles from electrocoating paint rinse waters.

In reverse osmosis membranes, the pores are so small, in the range 0.5–2 nm in diameter, that they are within the range of the thermal motion of the polymer chains. The most widely accepted theory of reverse osmosis transport considers the membrane to have no permanent pores at all. Reverse osmosis membranes are used to separate dissolved microsolutes, such as salt, from water. The principal application of reverse osmosis is the production of drinking water from brackish groundwater or seawater. Figure 22 shows the range of applicability of reverse osmosis, ultrafiltration, microfiltration, and conventional filtration. In some recent work, membranes that fall into the overlapping area between very retentive ultrafiltration membranes and very open ultrafiltration membranes are sometimes called nanofiltration membranes. The membranes have apparent pore diameters between 0.5 and 5 nm.

The fourth fully developed membrane process is electrodialysis, in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilizes an electrodialysis stack, built on the plate-and-frame principle, containing several hundred individual cells formed by a pair of anion- and cation-exchange membranes. The principal current application of electrodialysis is the desalting of brackish ground-water. However, industrial use of the process in the food industry, for example to deionize cheese whey, is growing, as is its use in pollution-control applications.

Of the two developing membrane processes listed in Table 3, gas separation and pervaporation, gas separation is the more developed. At least 20 companies worldwide offer industrial membrane-based gas separation systems for a variety of applications. In gas separation, a mixed gas feed at an elevated pressure is passed across the surface of a membrane that is selectively permeable to one component of the feed. The membrane separation process produces a permeate enriched in the more permeable species and a residue enriched in the less permeable species. Important, well-developed applications are the separation of hydrogen from nitrogen, argon, and methane in ammonia plants; the production of nitrogen from air; the separation of carbon dioxide from methane in natural gas operations; and the separation and recovery of organic vapors from air streams. Gas separation is an area of considerable current research interest; the number of applications is expected to increase rapidly over the next few years.

Pervaporation is a relatively new process with elements in common with reverse osmosis and gas separation. In pervaporation, a liquid mixture contacts one side of a membrane and the permeate is removed as a vapor from the other.

Currently, the only industrial application of pervaporation is the dehydration of organic solvents, in particular, the dehydration of 90–95% ethanol solutions, a difficult separation problem because an ethanol–water azeotrope forms at 95% ethanol. However, pervaporation processes are also being developed for the removal of dissolved organics from water and for the separation of organic solvent mixtures. These applications are likely to become commercial in the next decade.

The final membrane process listed in Table 3 is *facilitated transport*. No commercial plants are installed or are likely to be installed in the near future. Facilitated transport usually employs liquid membranes containing a complexing or carrier agent. The carrier agent reacts with one permeating component on the feed side of the membrane and then diffuses across the membrane to release the permeant on the product side of the membrane. The carrier agent is then reformed and diffuses back to the feed side of the membrane. The carrier agent thus acts as a shuttle to selectively transport one component from the feed to the product side of the membrane.

Facilitated transport membranes can be used to separate gases; membrane transport is then driven by a difference in the gas partial pressure across the membrane. Metal ions can also be selectively transported across a membrane driven by a flow of hydrogen or hydroxyl ions in the other direction. This process is sometimes called *coupled transport*.

Because the facilitated transport process employs a specific, reactive carrier species, very high membrane selectivities can be achieved. These selectivities are often far higher than those achieved by other membrane processes. This one fact has maintained interest in facilitated transport since the 1970s, but the problems of the physical instability of the liquid membrane and the chemical instability of the carrier agent are yet to be overcome.

5.1. Microfiltration.

Microfiltration is generally defined as the separation of particulates between 0.1 and 10 μm by a membrane. Two principal types of membrane filter are used: depth filters and screen filters. Figure 23 compares typical pore sizes of depth and screen filters. Screen filters have small pores in the top surface that collect particles larger than the pore diameter on the surface of the membrane. Depth filters have relatively large pores on the top surface and so particles pass to the interior of the membrane. The particles are then captured at constrictions in the membrane pores or by adsorption onto the pore walls. Screen filter membranes rapidly become plugged by the accumulation of retained particles at the top surface. Depth filters, which have a much larger surface area available to collect the particles, provide a greater holding capacity before fouling.

Depth filters are usually preferred for the most common type of microfiltration system, illustrated schematically in Figure 24**a**. In this process design, called *dead-end or in-line filtration*, the entire fluid flow is forced through the membrane under pressure. As particulates accumulate on the membrane surface or in its interior, the pressure required to maintain the required flow increases until, at some point, the membrane must be replaced. The useful life of the membrane is proportional to the particulate loading of the feed solution. In-line microfiltration of solutions as a final polishing step prior to use is a typical application.

Increasingly, screen membranes are preferred for the type of cross-flow microfiltration system shown in Figure 24**b**. Cross-flow systems are more complex than the in-line (dead-end) filter systems because they require a recirculation pump, valves, controls, etc. However, a screen membrane has a much longer lifetime than a depth membrane and, in principle, can be regenerated by back flushing. Cross-flow filtration is being adopted increasingly for microfiltration of high-volume industrial streams containing significant particulate levels (66).

The main microfiltration market is for in-line disposable cartridge filters. These cartridges are sold into two growing modern industries—microelectronics and pharmaceuticals—so prospects for continued market growth of the industry are very good. In addition to these existing markets, significant potential markets exist for microfiltration in bacterial control of drinking water, tertiary treatment of sewage, and replacement of diatomaceous earth depth filters in the chemical processing and food industries. The particle load of all these waters is far higher than that presently treated by microfiltration and has required development of cross-flow filtration systems able to give filter lifetimes of months or even years. Such systems are now being installed in municipal water treatment plants. The units can be cleaned by backflushing and offer reliable performance. Municipal water treatment is likely to develop into a major future application of microfiltration technology (68).

5.2. Ultrafiltration. The term ultrafiltration was coined in the 1920s to describe the collodion membranes available at that time. The process was first widely used in the 1960s when Michaels and others at Amicon Corp. adopted the then recently discovered Loeb-Sourirajan asymmetric membrane preparation technique to the production of ultrafiltration membranes (26). These membranes had pore sizes in the range 2–20 nm and found an immediate application in concentrating and desalting protein solutions in the laboratory. Later, Romicon, Abcor, and other companies developed the technology for a wide range of industrial applications. Early and still important applications were the recovery of electrocoat paint from industrial coating operations and the clarification of emulsified oily wastewaters in the metalworking industry. More recent applications are in the food industry for concentration of proteins in cheese production and for juice clarification (67). A good review of ultrafiltration application is given in Ref. 67. The current ultrafiltration market is in the range $150–250 million/year.

Ultrafiltration membranes are usually asymmetric membranes made by the Loeb-Sourirajan process. They have a finely porous surface or skin supported on a microporous substrate. The membranes are characterized by their *molecular weight cutoff*, a loosely defined term generally taken to mean the molecular weight of the globular protein molecule that is 95% rejected by the membrane. A series of typical molecular weight cutoff curves are shown in Figure 25. Globular proteins are usually specified for this test because the rejection of linear polymer molecules of equivalent molecular weight is usually much less. Apparently, linear, flexible molecules are able to snake through the membrane pores, whereas rigid globular molecules are retained.

A key factor determining the performance of ultrafiltration membranes is concentration polarization, which causes membrane fouling due to deposition of retained colloidal and macromolecular material on the membrane surface.

The pure water flux of ultrafiltration membranes is often very high—more than 1 $cm^3/(cm^2{\cdot}min)$ [350 $gal/(ft^2{\cdot}day)$]. However, when membranes are used to separate macromolecular or colloidal solutions, the flux falls within seconds, typically to the 0.1 $cm^3/(cm^2{\cdot}min)$ level. This immediate drop in flux is caused by the formation of a gel layer of retained solutes on the membrane surface because of the concentration polarization. The gel layer forms a secondary barrier to flow through the membrane, as illustrated in Figure 26. This first decline in flux is determined by the composition of the feed solution and its fluid hydrodynamics. Sometimes the resulting flux is constant for a prolonged period, and when the membrane is retested with pure water, its flux returns to the original value. More commonly, however, a further slow decline in flux occurs over a period of hours to weeks, depending on the feed solution. Most of this second decrease in flux is caused by slow consolidation of the secondary layer formed by concentration polarization on the membrane surface. Formation of this consolidated gel layer, called *membrane fouling*, is difficult to control. Control techniques include regular membrane cleaning, back flushing, or using membranes with surface characteristics that minimize adhesion. Operation of the membrane at the lowest practical operating pressure also delays consolidation of the gel layer.

A typical plot illustrating the slow decrease in flux that can result from consolidation of the secondary layer is shown in Figure 27. The pure water flux of these membranes is approximately 200 L/min, but on contact with an electrocoat paint solution containing 10–20% latex, the flux immediately falls to about 40–50 L/min. This first drop in flux is due to the formation of the gel layer of latex particles on the membrane surface, as shown in Figure 26. Thereafter, the flux declines steadily over a 2-week period. This second drop in flux is caused by slow densification of the gel layer under the pressure of the system. In this particular example the densified gel layer could be removed by periodic cleaning of the membrane. When the cleaned membrane is exposed to the latex solution again, the flux is restored to that of a fresh membrane.

If the regular cleaning cycle shown in Figure 27 is repeated many times, the membrane flux eventually does not return to the original value on cleaning. Part of this slow, permanent loss of flux is believed to be due to precipitates on the membrane surface that are not removed by the cleaning procedure. A further cause of the permanent flux loss is believed to be internal fouling of the membrane by material that penetrates the membrane pores and becomes lodged in the interior of the membrane, as illustrated in Figure 26.

As described previously, the initial cause of membrane fouling is concentration polarization, which results in deposition of a layer of material on the membrane surface. In ultrafiltration, solvent and macromolecular or colloidal solutes are carried toward the membrane surface by the solution permeating the membrane. Solvent molecules permeate the membrane, but the larger solutes accumulate at the membrane surface. Because of their size, the rate at which the rejected solute molecules can diffuse from the membrane surface back to the bulk solution is relatively low. Thus their concentration at the membrane surface increases far above the feed solution concentration. In ultrafiltration the concentration of retained macromolecular or colloidal solutes at the membrane surface is typically 20–50 times higher than the feed solution concentration. These solutes become so concentrated at the membrane surface that a gel layer is formed and becomes a secondary barrier to flow through the membrane. The formation of the gel layer is easily modeled mathematically and is reviewed in detail elsewhere (67,69–71). One consequence of the formation of the gel layer on the membrane surface is that ultrafiltration membrane fluxes reach a limiting plateau value that cannot be exceeded at any particular operating condition.

The effect of the gel layer on the flux through an ultrafiltration membrane at different feed pressures is illustrated by the experimental data in Figure 28.

Experience has shown that the best long-term performance of an ultrafiltration membrane is obtained when the applied pressure is maintained at or just below the plateau pressure p_3 shown in Figure 28. Operating at higher pressures does not increase the membrane flux but does increase the thickness and density of retained material at the membrane surface layer. Over time, material on the membrane surface can become compacted or precipitate, forming a layer of deposited material that has a lower permeability; the flux then falls from the initial value.

The high cost per gallon of permeate produced limits the expansion of ultrafiltration into most large wastewater and industrial process stream applications. Cost are high because membrane fluxes are modest, large amounts of energy are used to circulate the feed solution to control fouling, membrane modules must be cleaned frequently, and membrane lifetimes are short.

Only limited progress in controlling the problems of membrane fouling and gel layer formation (68) has been made in the last 20 years and, barring an unexpected breakthrough, progress is likely to remain slow. Development of inherently fouling-resistant membranes by changing the membrane surface absorption characteristics or charge is a promising approach. By reducing adhesion of the deposited gel layer to the surface, the scrubbing action of the feed solution can be enhanced. Another approach is to develop inherently more fouling-resistant modules. In principle, bore-side-feed capillary fiber modules offer high membrane areas, good flow distribution, and the potential for simple automatic flushing to clean the membrane. The capillary fibers used to date have generally been limited to relatively small diameters and low operating pressures. Development of economical ways to produce 2- to 3-mm-diameter capillary fiber modules, able to operate at 50–100 psi, could lead to lower energy consumption and higher, more stable membrane fluxes. Monolithic ceramic membrane modules have all of these features, but for these to be widely accepted, costs must be reduced by an order of magnitude from today's levels, that is, to less than US\$100–200/m^2. If this cost reduction were achieved, ceramics might replace polymeric membranes in many applications. Vibrating membrane modules have been introduced recently and, although costs are high, their performance is very good. Cost reduction could make this type of module more generally applicable in the future.

5.3. Reverse Osmosis. This was the first membrane-based separation process to be commercialized on a significant scale. As described previously, the breakthrough discovery that made reverse osmosis possible was the development of the Loeb–Sourirajan asymmetric cellulose acetate membrane. This membrane made desalination by reverse osmosis practical; within a few years commercial plants were installed. Currently, the total worldwide market for reverse osmosis membrane modules is about \$300 million/year, split approximately between 15%

hollow-fiber and 85% spiral-wound modules. The general trend of the industry is toward spiral-wound modules for this application, and the market share of the hollow-fiber products is falling (72).

The first reverse osmosis modules made from cellulose diacetate had a salt rejection of approximately 97–98%. This was enough to produce potable water (ie, water containing less than 500-ppm salt) from brackish water sources, but was not enough to desalinate seawater efficiently. In the 1970s, interfacial composite membranes with salt rejections greater than 99.5% were developed, making seawater desalination possible (28,29); a number of large plants are operating worldwide.

Although the principal application of reverse osmosis membranes is still desalination of brackish water or seawater to provide drinking water, a recent, significant market is production of ultrapure water by filtration of municipal drinking water. Such water is used in the electronics industry, where huge amounts of extremely pure water with a total salt concentration significantly below 1 ppb are required to wash silicon wafers.

A simplified flow scheme for a brackish water reverse osmosis plant is shown in Figure 29. In this example, it is assumed that the brackish water is heavily contaminated with suspended solids, so flocculation followed by a sand filter and a cartridge filter are used to remove particulates. The pH of the feed solution might be adjusted, followed by chlorination to sterilize the water to prevent bacterial growth on the membranes and addition of an antiscalant to inhibit precipitation of multivalent salts on the membrane. Finally, if chlorine-sensitive interfacial composite membranes are used, sodium sulfite is added to remove excess chlorine before the water contacts the membrane. Generally, more pretreatment is required in plants using hollow-fiber modules than in plants using spiral-wound modules. This is one reason why hollow-fiber modules have been displaced by spiral-wound systems in most brackish water installations.

A feature of the system design shown in Figure 29 is the staggered arrangement of the module pressure vessels. As the volume of the feed water is reduced as water is removed in the permeate, the number of modules arranged in parallel is also reduced. In the example shown, the feed water passes initially through four modules in parallel, then through two, and finally through a single module in series. This is called a *Christmas tree or tapered module design* and provides a high average feed solution velocity through the modules.

The operating pressure of reverse osmosis systems has gradually fallen over the past 20 years as the permeability and rejections of membranes have steadily improved. The first plants operated at pressures up to 60 atm, but typical brackish water plants now operate at pressures in the 10- to 20-atm range.

The reverse osmosis industry is now well established. The market is divided among three or four large manufacturers, who produce 70% of the membrane modules, and a much larger number of system builders. The system builders buy modules almost as commodities from the various suppliers according to their particular needs. The demand for reverse osmosis systems to produce ultrapure water for the electronics and pharmaceutical industries is very strong. Municipalities in arid regions of the world are also continuing to buy brackish water and some seawater desalination units.

Many incremental improvements have been made to membrane and module performance over the past 20 years, resulting in steadily decreasing water desalination costs in inflation-adjusted dollars. Since 1980, just after the introduction of the first interfacial composite membranes, the cost of spiral-wound membrane modules on a per square meter basis has decreased seven-fold. At the same time the water flux has doubled, and the salt permeability has decreased seven-fold. Taking these improvements into account, today's membranes are almost 100 times better than those of the 1980s. This type of incremental improvement is likely to continue for some time.

The key short-term technical issue is the limited chlorine resistance of interfacial composite membranes. A number of incremental steps made over the past 10−15 years have improved resistance, but current chlorine-resistant interfacial composites do not have the rejection and flux of the best conventional membranes. All the major membrane manufactures are working on this problem. Three longer-term, related technical issues are fouling resitance, pretreatment, and membrane cleaning. Current membrane modules are subject to fouling by particulates and scale; this fouling can only be controlled by good (and expensive) feed water pretreatment and by membrane cleaning. In some large potential reverse osmosis markets, such as municipal wastewater reclamation and industrial process water treatment, the complexity, expense, and low reliability due to membrane fouling limit expansion significantly.

A further long-term area of research is likely to be the development of reverse osmosis membranes to recover organic solutes from water (68).

5.4. Electrodialysis. Electrodialysis is an electrochemical separation process in which a gradient in electrical potential is used to separate ions with charged, ionically selective membranes. A schematic of the simplest type of electrodialysis system is shown in Figure 30 (73–75). The process uses an electrodialysis stack, built on the plate-and-frame principle and containing several hundred cells each formed by a pair of anion- and cation-exchange membranes. Anion-exchange membranes contain fixed, positively charged entities, such as quaternary ammonium groups, fixed to the polymer backbone. These membranes are permeable to negatively charged ions, but positive ions are excluded from permeation by the fixed charges. Similarly, cation-exchange membranes contain fixed, negatively charged groups, such as sulfonic acid groups. Cationic membranes are permeable to positively charged ions, but not to negatively charged ions. The arrangement of the membranes in an electrodialysis stack is such that every second cell becomes depleted of salt, while the adjacent cells become concentrated in salt. The degree of concentration is determined by the rate of flow of solution through the stack.

Electrodialysis is used widely to desalinate brackish water, but this is by no means its only significant application. In Japan, which has no readily available natural salt brines, electrodialysis is used to concentrate salt from seawater. The process is also used in the food industry to deionize cheese whey, and in a number of pollution-control applications.

In the past, the principal problem inhibiting the use of electrodialysis was slow deterioration of the membranes by chemical degradation and scaling. In the 1970s the introduction of a process called *polarity reversal* reduced the scaling problem significantly. In this process, the flow of current through the electrodialysis stack is reversed periodically by reversing the polarity of the electrodes. When the polarity of the electrodes is reversed, the concentrated stream becomes the demineralized product stream and the demineralized stream becomes the concentrated stream; automatic valves are used to switch the streams. When the current is reversed, scale deposited on the membranes in the previous cycle is dissolved. Typically, the current of an electrodialysis stack is reversed every 15–20 min. One or two minutes production of the system is lost after each reversal, but the reduced scaling and fouling of the membranes more than compensates for this loss in productivity. One of the most attractive features of electrodialysis is its energy efficiency.

5.5. Gas Separation. During the 1980s, gas separation using membranes became a commercially important process; the size of this application is still increasing rapidly. In gas separation, one of the components of the feed permeates a selective membrane at a much higher rate than the others. The driving force is the pressure difference between the pressurized feed gas and the lower pressure permeate.

Both porous and dense membranes can be used as selective barriers; Figure 31 illustrates the mechanism of gas permeation through both classes. Three types of porous membranes, differing in pore size, are shown. If the pores are relatively large, in the range 0.1–10 μm, gases permeate the membrane by convective flow, and no separation occurs. If the pores are smaller than 0.1 μm, then the pore diameter is the same size or smaller than the mean free path of the gas molecules. Diffusion through such pores is governed by Knudsen diffusion, and the transport rate of different gases is inversely proportional to the square root of the molecular weight. The latter relationship, sometimes called *Graham's law of diffusion*, was exploited on a massive scale in the separation of $U^{235}F_6$ and $U^{238}F_6$ during the Manhattan Project. Finally, if the membrane pores are very small indeed, of the order 0.5–2 nm, then molecules are separated by molecular sieving. Actual transport mechanisms through this type of membrane are complex and include both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). Nonetheless, ceramic and ultramicroporous carbon membranes have been prepared with extraordinarily high separations for very similar molecules (47–49). Although microporous membranes are a topic of research interest, all current commercial gas separations are based on the fourth type of mechanism shown in Figure 31.

The second factor affecting the overall membrane selectivity is the sorption or solubility selectivity. The sorption coefficient of gases and vapors, which is a measure of the energy required for the permeant to be sorbed by the polymer, increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter, because large molecules are normally more condensable than small ones. The Henry's law sorption coefficient can, therefore, be plotted against boiling point or molar volume as shown in Figure 32 (76). As the figure shows, sorption selectivity favors the larger, more condensable molecules, such as hydrocarbon vapors, over the permanent gases, such as oxygen and nitrogen. The difference between the sorption coefficients of permeants in rubbery and glassy polymers is far less marked than the differences in the diffusion coefficients.

Both hollow-fiber and spiral-wound modules are used in gas separation applications. Spiral-wound modules are favored if the gas stream contains oil mist or condensable vapors as in the separation of hydrocarbon vapors from nitrogen or hydrogen or in natural gas separations. The first large-scale commercial application of gas separation was the separation of hydrogen from nitrogen in ammonia purge gas streams, launched in 1980 by Permea (now a division of Air Products). This process was followed by a number of similar applications, such as hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo-chemical synthetic plants. Several hundred of these plants have now been installed.

Following Permea's success, several companies produced membrane systems to treat natural gas streams, particularly to separate carbon dioxide from methane. The goal is to produce a stream containing less than 2% carbon dioxide to be sent to the national pipeline and a permeate enriched in carbon dioxide to be flared or reinjected into the ground. Cellulose acetate is the most widely used membrane material for this separation, but because its carbon dioxide/methane selectivity is only about 15, two-stage systems are often required to achieve a sufficient separation. The membrane process is generally best suited to relatively small streams, but the economics have slowly improved over the years and more than 100 natural gas treatment plants have now been installed—some quite large. Figure 33 shows flow schematics for one-stage and two-stage carbon dioxide membrane separation plants.

The application of membranes to gas separation problems has grown rapidly. The current status of membrane gas separation processes is summarized in Table 4, in which the processes are divided into four groups. The first group consists of the established processes: nitrogen production from air, hydrogen recovery and air drying. These processes represent more than 80% of the current gas separation membrane market. All have been used on a large commercial scale for 10 years, and dramatic improvements in membrane selectivity, flux and process designs have been made during that time. For example, today's hollow fine fiber nitrogen production module generates more than 10 times the amount of nitrogen, with better quality and at a lower energy consumption, than the modules produced in the early 1980s. However, the technology has now reached a point at which, barring a completely unexpected breakthrough, further changes in productivity are likely to be the result of a number of small incremental changes.

Developing processes are the second group of applications. These include carbon dioxide separation from natural gas, organic vapor separation from air and nitrogen, and recovery of light hydrocarbons from refinery and petrochemical plant purge gases. All of these processes are performed on a commercial scale, and in total several hundred plants have been installed. Significant expansion in these applications, driven by the development of better membranes and process designs, is occurring. For example, carbon dioxide removal from natural gas has been practiced using cellulose acetate membranes for more than 15 years. Introduction of more selective and higher-flux membranes has begun and, in time, is likely to make membrane processes much more competitive with amine absorption. The application of silicone rubber vapor separation membranes in petrochemical and refinery applications is currently growing.

The "to be developed" membrane processes represent the future expansion of gas separation technology. Natural gas treatment processes, including dehydration, natural gas liquids (C_{3+} hydrocarbons) recovery, and hydrogen sulfide removal, are currently being studied at the field testing and early commercial stage by several companies. The market is very large, but the fraction that membranes will ultimately capture is unknown. The production of oxygen-enriched air is another large potential application for membranes. The market size depends completely on the properties of the membranes that can be produced. Improvements of a factor of two in flux at current oxygen/nitrogen selectivities would probably produce a limited membrane market; improvements by a factor of five to ten would make the use of oxygen-enriched air in natural gas combustion processes attractive. In this case the market could be very large indeed. The final application listed in Table 4 is the separation of organic vapor mixtures using membranes in competition, or perhaps in combination, with distillation (68).

5.6. Pervaporation. In this separation process, illustrated schematically in Figure 34, a multicomponent liquid stream is passed across a membrane that preferentially permeates one or more of the components. As the feed liquid flows across the membrane surface, the preferentially permeated component passes through the membrane as a vapor. Transport through the membrane is induced by maintaining a vapor pressure on the permeate side of the membrane that is lower than the vapor pressure of the feed liquid. The pressure difference is achieved by cooling the permeate vapor to below the temperature of the feed stream, causing it to condense. This spontaneously generates a partial vacuum on the permeate side of the membrane. The condensate is then removed as a concentrated permeate fraction; the residue, depleted of the permeating component, exits on the feed side of the membrane. The process can be applied to the removal of dissolved water from organic solvents, to the extraction of organic solvents from water, and to the separation of mixed organic solvents.

The selectivity of pervaporation membranes varies considerably and has a critical effect on the overall separation obtained. The range of results that can be obtained for the same solutions and different membranes is illustrated in Figure 35 for the separation of acetone from water using two types of membrane (77,78). The figure shows the concentration of acetone in the permeate as a function of the concentration in the feed. The two membranes shown have dramatically different properties. The silicone rubber membrane removes acetone selectively, whereas the cross-linked PVA membrane removes water selectively. This difference occurs because silicone rubber is hydrophobic and rubbery, thus permeates the acetone preferentially. On the other hand, PVA is hydrophilic and glassy, thus permeates the small hydrophilic water molecules preferentially.

A flow scheme for an integrated distillation–pervaporation plant operating on a 5 wt% ethanol feed from a fermentation mash is shown in Figure 36. The distillation column produces an ethanol stream containing 85–90 wt% ethanol, which is fed to the pervaporation system. To maximize the vapor pressure difference across the membrane, the pervaporation module usually operates at a temperature of 80°C with a corresponding feed stream vapor pressure of 400–600 kPa (4–6 atm). Despite these harsh conditions, the membrane lifetime is good and qualified guarantees for up to four years are given.

Figure 36 shows a single-stage pervaporation unit. In practice, at least three pervaporation stages are used in series, with additional heat being supplied to the ethanol feed between each stage. This compensates for pervaporative cooling of the feed and maintains the feed at 80°C. The heat required is obtained by thermally integrating the pervaporation system with the condenser of the final distillation column. Most of the energy used in the process is, therefore, low grade heat. Generally, about 0.5 kg of steam is required for each kilogram of ethanol produced. The energy consumption of the pervaporation process is, therefore, about 559 kJ/L (2000 Btu/gal) of product, less than 20% of the energy used in azeotropic distillation, which is typically in the range 3–3.4 MJ/L (11,000–12,000 Btu/gal). Moreover, pervaporation uses very low grade steam, which is available in most industrial plants at very low cost.

Although most of the installed solvent dehydration systems have been for ethanol dehydration, dehydration of other solvents, including isopropanol, glycol, acetone, and methylene chloride, has been considered.

Currently, the main industrial application of pervaporation is the dehydration of organic solvents, in particular, the dehydration of 90–95% ethanol solutions, a difficult separation problem because of the ethanol–water azeotrope at 95% ethanol. Pervaporation membranes that selectively permeate water can produce more than 99.9% ethanol from these solutions. Pervaporation processes are also being developed for the removal of dissolved organics from water and for the separation of organic mixtures (68).

5.7. Other Membrane Separation Techniques. The six membrane separation processes described earlier represent the bulk of the industrial membrane separation industry. A seventh process, dialysis, is used on a large scale to remove toxic metabolites from blood in patients suffering from kidney failure (79). The first successful artificial kidney was based on cellophane (regenerated cellulose) membranes and was developed by W.J. Kolf in 1945. Over the past 50 years, many changes have been made. Currently, most artificial kidneys are based on hollow-fiber modules having a membrane area of about 1 m^2. Cellulose fibers are still widely used, but are gradually being displaced by fibers made from polycarbonate, polysulfone, and other polymers, which have higher fluxes or are less damaging to the blood. As shown in Figure 37, blood is circulated through the center of the fiber, while isotonic saline, the dialysate, is pumped countercurrently around the outside of the fibers. Urea, creatinine, and other low molecular weight metabolites in the blood diffuse across the fiber wall and are removed with the saline solution. The process is quite slow, usually requiring several hours to remove the required amount of the metabolite from the patient, and must be repeated one to two times per week. Nonetheless, 100,000 patients use these devices on a regular basis.

In terms of membrane area used and dollar value of the membrane produced, artificial kidneys are the single largest application of membranes. Similar hollow-fiber devices are being explored for other medical uses, including an artificial pancreas, in which islets of Langerhans supply insulin to diabetic patients, or an artificial liver, in which adsorbent materials remove bilirubin and other toxins.

One other membrane separation technique, yet to be used on a commercial scale, is carrier facilitated transport. In this process, the membrane used to perform the separation contains a carrier which preferentially reacts with one of the components to be transported across the membrane. Most of the work on carrier facilitated transport has employed liquids containing a dissolved complexing agent (58,59). Membranes are formed by holding the liquids by capillary action in the pores of a microporous film. The carrier agent reacts with one permeating component on the feed side of the membrane and then diffuses across the membrane to release the permeant on the product side of the membrane. The carrier agent is then reformed and diffuses back to the feed side of the membrane. Thus, the carrier agent acts as a selective shuttle to transport one component from the feed to the product side of the membrane. Facilitated transport membranes can be used to separate gases; membrane transport is then driven by a difference in the gas partial pressure across the membrane. Metal ions can also be transported selectively across a membrane, driven by a flow of hydrogen or hydroxyl ions in the opposite direction; this process is sometimes called coupled transport. Examples of facilitated transport processes for gas and metal ion transport are shown in Figure 38.

Because the facilitated transport process employs a reactive carrier species, very high membrane selectivities can be achieved. These selectivities are often far larger than those achieved by other membrane processes, a factor that has maintained interest in facilitated transport. However, no significant commercial applications exist or are likely to exist in the next decade. The principal problems are the physical instability of the membrane and the chemical instability of the carrier agent.

5.8. Membrane Contactors.

In the membrane processes described earlier, the membrane acts as a selective barrier, allowing relatively free passage of one component while retaining another. In membrane contactors the membrane functions as an interface between two phases but does not control the passage of permeants across the membrane (13,14). Delivery or removal of gases from liquids is the largest application of contactors.

One example is the blood oxygenator used during surgery when the patient's lungs cannot function normally. A flow schematic of one of these hollow-fiber devices is shown in Figure 39. More than 1 million procedures per year use blood oxygenators. Each device costs about $500–600, so the total annual market is about $500 million.

Membrane contactors have also found some industrial applications, most commonly to deoxygenate ultrapure water for the electronics industry (80) or for boiler feed water and to adjust carbonation levels in beverages (81). Microporous hollow-fiber membrane modules are most commonly used. The aqueous phase is circulated on the shell side of the fiber and a gas sweep or vacuum flows down the inside of the fibers.

5.9. Controlled Drug Delivery.

A significant application of membranes is to moderate the release of biologically active agents, such as insecticides, fertilizers, and most importantly, drugs. Although the concept of controlled drug release using a rate-controlling membrane to moderate drug delivery can be traced to the 1950s, the founding of the Alza Corp. in the late 1960s gave the entire technology a decisive thrust. The products developed by Alza during the subsequent 25 years stimulated the entire pharmaceutical industry (82,83).

Controlled release can be achieved by a wide range of techniques; a simple example, a transdermal patch, is illustrated in Figure 40. In this device, a drug is held in a reservoir surrounded by a membrane. With such a system, the release rate of drug is constant as long as a constant concentration of drug is maintained within the device. Such a constant concentration is maintained if the reservoir contains a saturated solution and sufficient excess of solid drug. Systems that operate by this principle are commonly used in transdermal patches to moderate delivery of drugs such as nitroglycerine (for angina), nicotine (for smoking cessation), and estradiol (for hormone replacement therapy) through the skin. Other devices using osmosis or biodegradation as the rate-controlling mechanism are also produced as implants and tablets.

6. Membrane Reactor Applications

Membrane-based reactive separation processes, in which membrane separation is coupled with a catalytic reaction in one unit, are rather attractive applications because they are potentially compact, less capital intensive, and have lower processing costs than traditional processes. Moreover, they often enhance selectivity and yield (84). Applications range from catalytic reactions like hydrocabon dehydrogenation, to hormone synthesis, to the biological treatment of wastewaters. The enormous potential of large-scale applications in the oil and petrochemical industry promises major advances in the developments of such systems in the near future.

Various types, shapes, and configurations of catalytically active and inactive membranes are employed in catalytic membrane-based reactive separations processes (85–87). This is because reactor yield and reaction selectivity depend typically not only on common process parameters but also on membrane characterisitcs.

Membrane based reactive separations are advantageous in applications such as dehydrogenation and esterification for which the continuous extraction of products enhances the yield by shifting the equilibrium. They are quite attractive also for processes of other types of reactions, including hydrogenation, and partial and total oxidation, in which the use of membranes has shown to increase the yield and selectivity.

In biotechnological applications, membrane processes are coupled with industrially important biological reactions, for example, in fermentation of amino acids, antibiotics, and other fine chemicals. Here the advantage is the continuous elimination of metabolites allowing for high reactor productivity. In other applications bacteria, enzymes, or animal cells are immobilization onto the membrane and used to produce high value chemicals and pharmaceuticals. Reactive separation processes are currently finding use in biological treatment of contaminated air and water streams (84).

Low temperature applications, including bio-production of fine chemicals, pervaporation, and wastewater treatment are currently in use and proved economical. This is mainly because they employ polymeric and macroporous or mesoporous inorganic membranes, which are well characterized and readily available, and require relatively simpler configuration. Some progress has been made also in a number of large-scale, high temperature applications. However, further progress depends on the development of more stable and affordable membranes as well as careful process design and reactor analysis.

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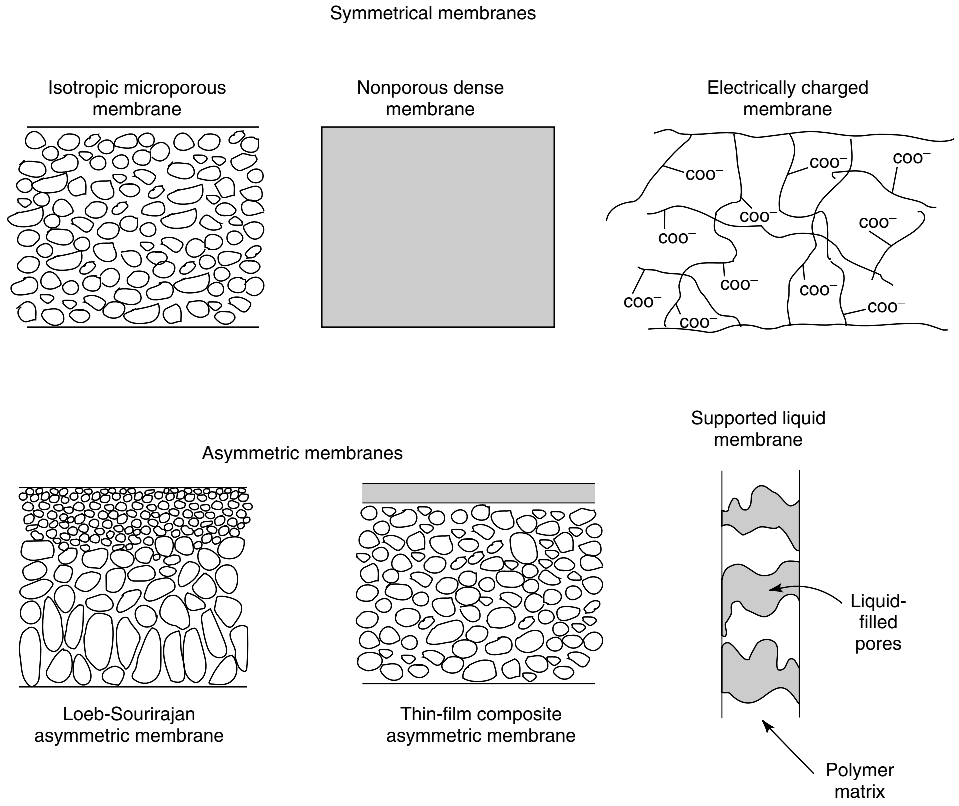


Fig. 1. Schematic diagrams of the principal types of membrane.

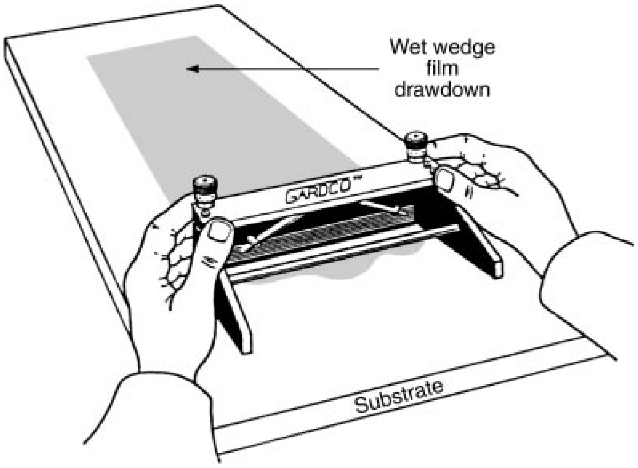


Fig. 2. A typical hand-casting knife. (Courtesy of Paul N. Gardner Co., Inc.)

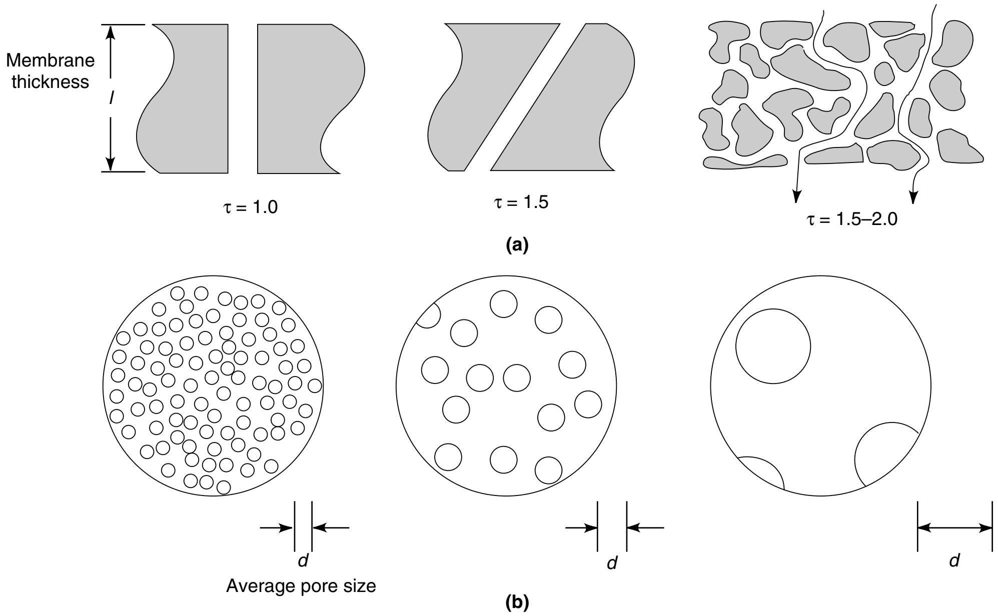


Fig. 3. Microporous membranes are characterized by tortuosity, τ, porosity, ϵ, and their average pore diameter, d. (**a**) Cross-sections of porous membranes containing cylindrical pores. (**b**) Surface views of porous membranes of equal ϵ, but differing pore size.

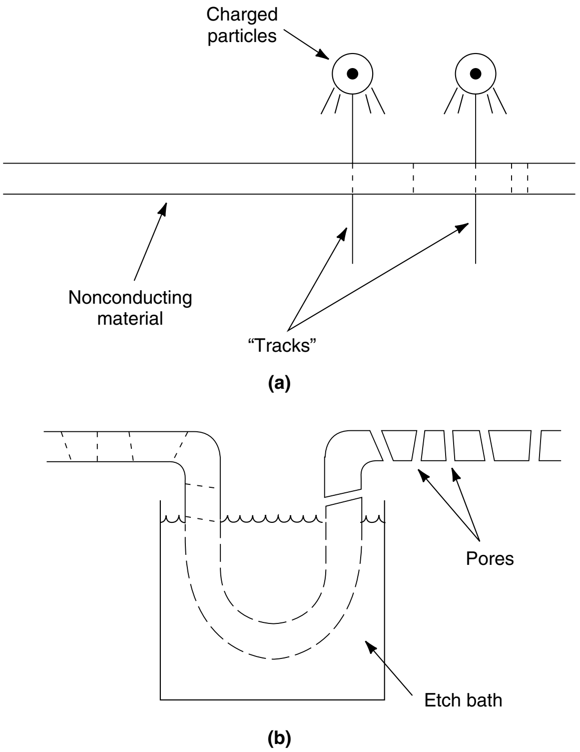


Fig. 4. Diagram of the two-step process to manufacture nucleation track membranes. (**a**) Polycarbonate film is exposed to charged particles in a nuclear reactor. (**b**) Tracks left by particles are preferentially etched into uniform cylindrical pores (8). (Courtesy of Corning Costar Corp., Nucleopore Division.)

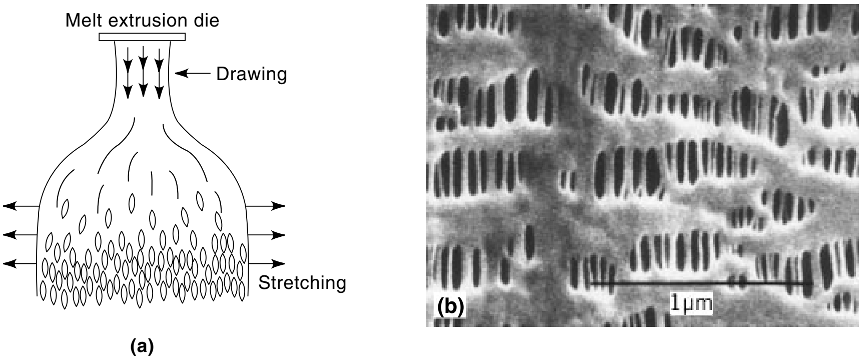


Fig. 5. (**a**) Preparation method and (**b**) scanning electron micrograph of a typical expanded polypropylene film membrane, in this case Celgard. (Courtesy of Hoechst-Celanese Corp., Separation Products Division.)

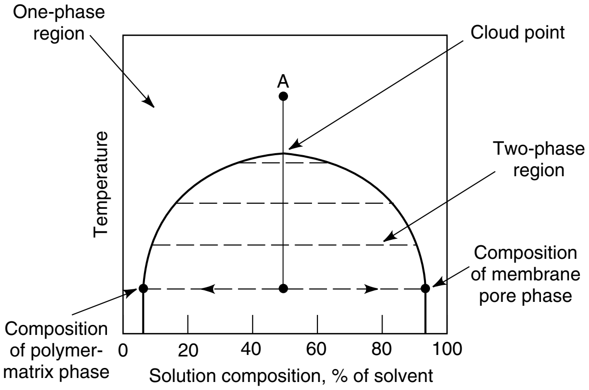


Fig. 6. Phase diagram showing the composition pathway traveled by the casting solution during precipitation by cooling. Point A represents the initial temperature and composition of the casting solution. The cloud point is the point of fast precipitation. In the two-phase region tie lines linking the precipitated polymer phase and the suspended liquid phase are shown.

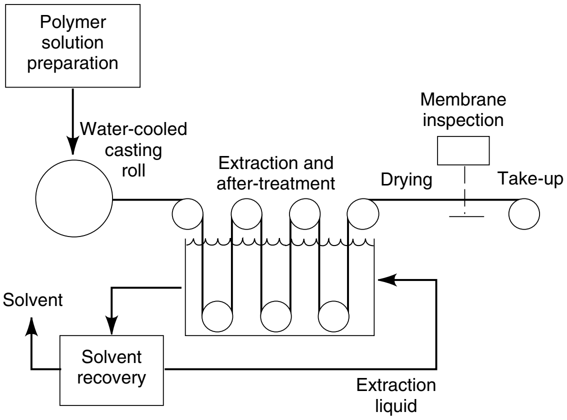
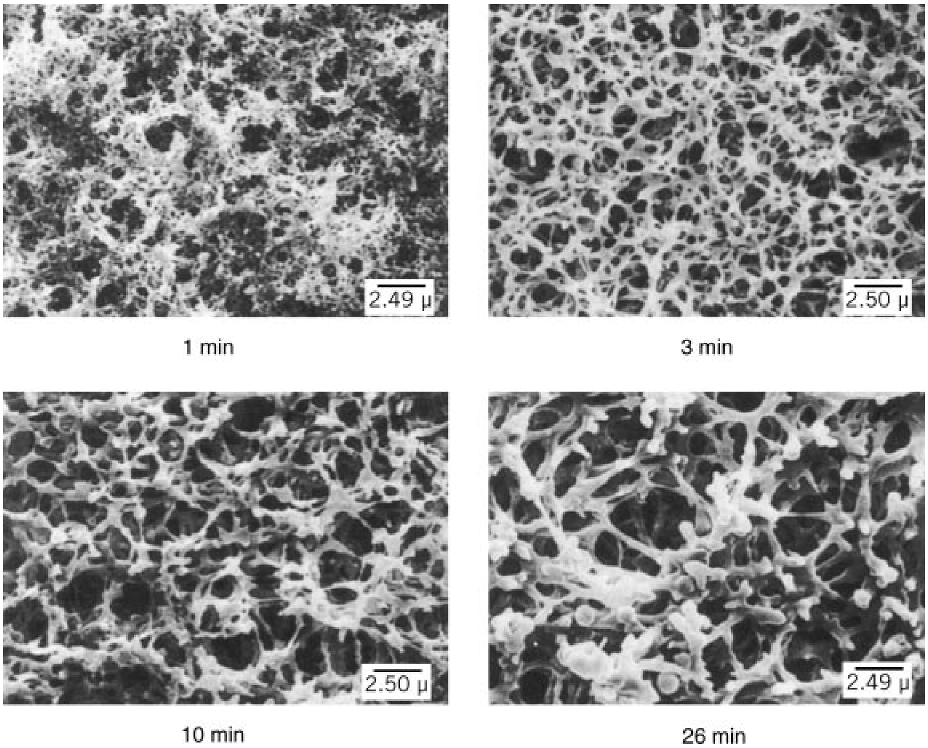


Fig. 7. Equipment to prepare microporous membranes by the polymer precipitation by cooling technique (23).



1 min

3 min

10 min

26 min

Fig. 8. SEM photographs of cellulose acetate membranes cast from a solution of acetone (volatile solvent) and 2-methyl-2,4-pentanediol (nonvolatile solvent). The evaporation time before the structure is fixed by immersion in water is shown (24).

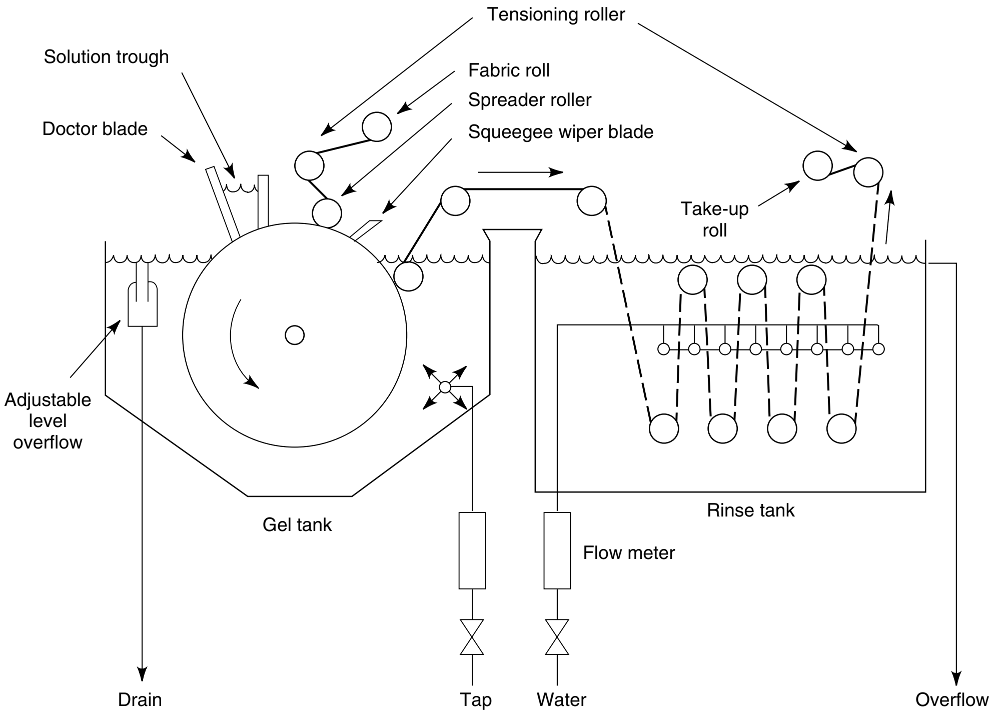


Fig. 9. Schematic of Loeb-Sourirajan membrane casting machine used to prepare reverse osmosis or ultrafiltration membranes. A knife and trough is used to coat the casting solution onto a moving fabric or polyester web which enters the water-filled gel tank. After the membrane has formed, it is washed thoroughly to remove residual solvent before being wound up.

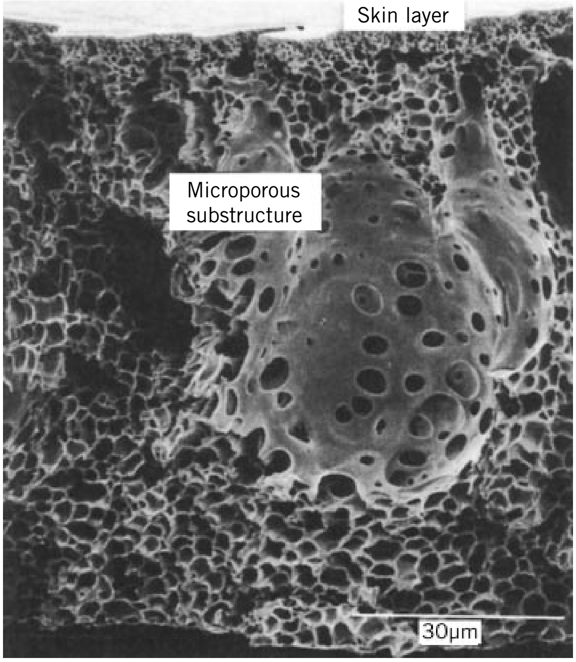


Fig. 10. Scanning electron micrograph of an asymmetric Loeb-Sourirajan membrane. (Courtesy of Membrane Technology and Research, Inc.)

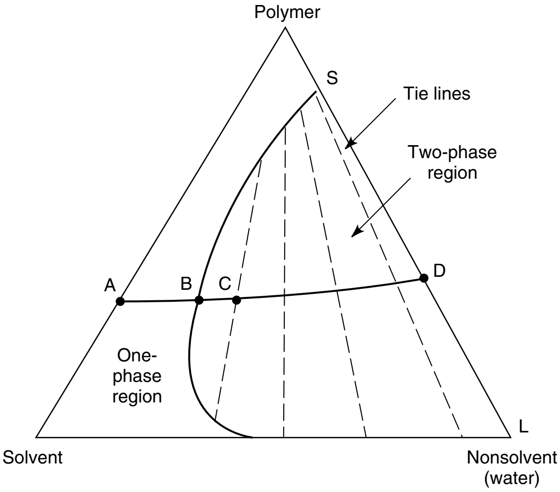


Fig. 11. Phase diagram showing the composition pathway traveled by a casting solution during the preparation of porous membranes by solvent evaporation. A, initial casting solution; B, point of precipitation; and C, point of solidification. See text.

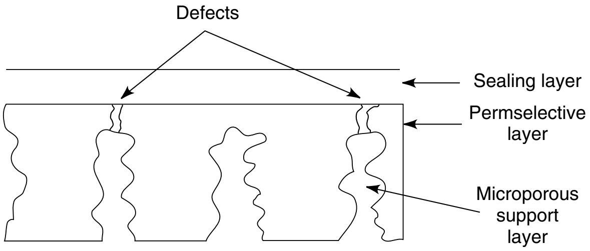


Fig. 12. Schematic of coated gas-separation membranes (6).

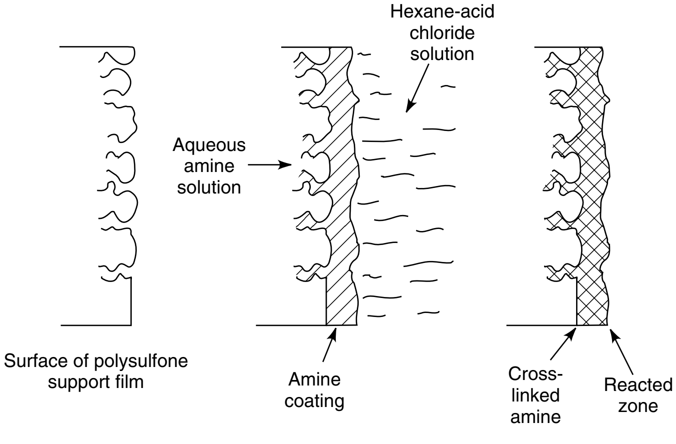


Fig. 13. Schematic of the interfacial polymerization process. The microporous film is first impregnated with an aqueous amine solution. The film is then treated with a multivalent cross-linking agent dissolved in a water-immiscible organic fluid, such as hexane or Freon-113. An extremely thin polymer film forms at the interface of the two solutions.

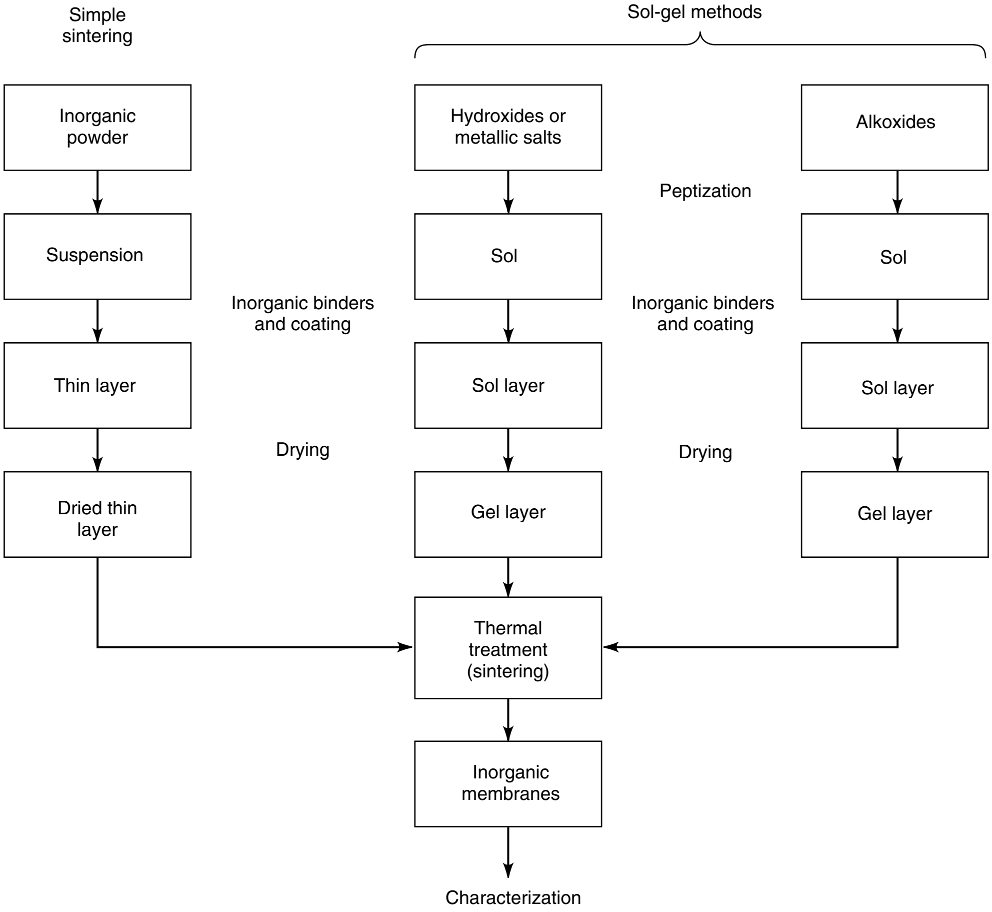


Fig. 14. Sol–gel and simple sintering process used to make ceramic membranes.

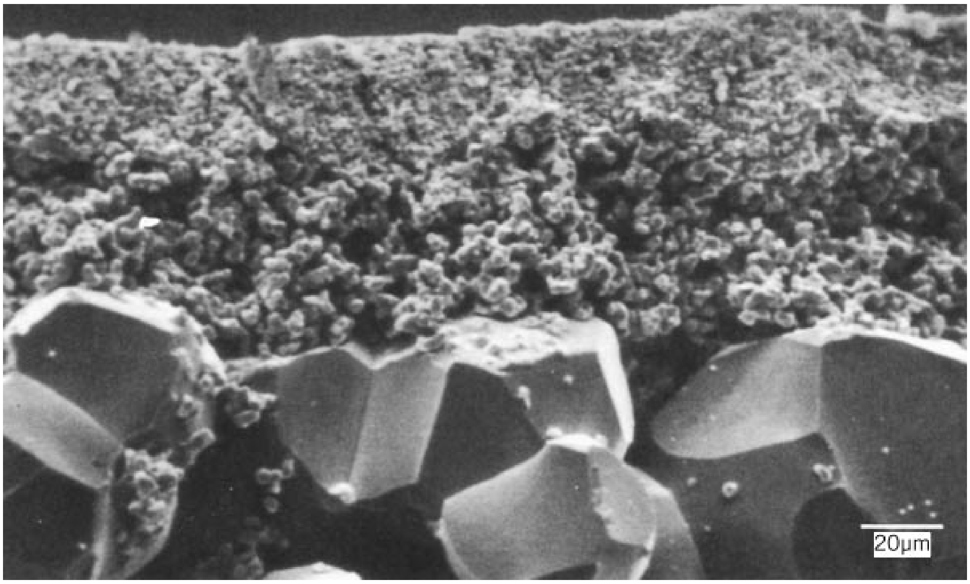


Fig. 15. Cross-sectional scanning electron micrograph of a three-layered alumina membrane/support (pore sizes 0.2, 0.8, and 12 μm, respectively). (Courtesy of U.S. Filter Corp.)

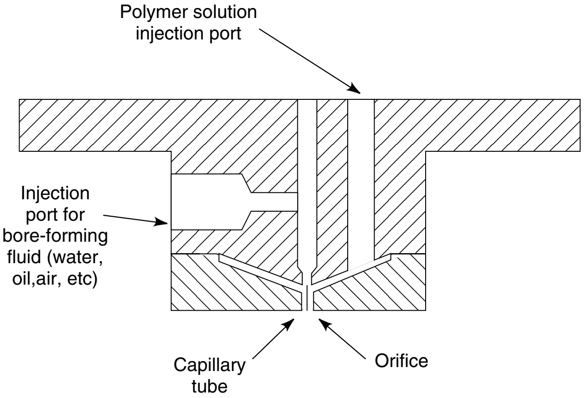


Fig. 16. Twin-orifice spinnerette design used in solution-spinning of hollow-fiber membranes. Polymer solution is forced through the outer orifice, while bore-forming fluid is forced through the inner capillary.

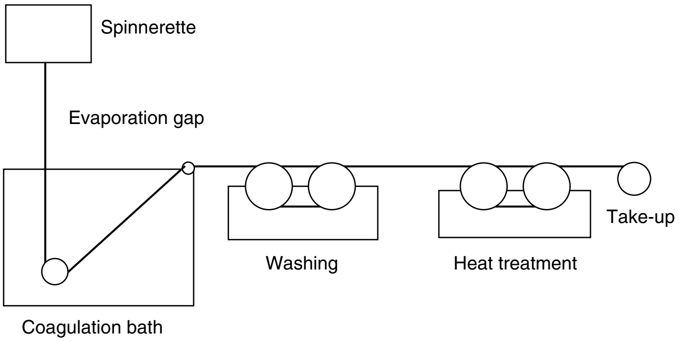


Fig. 17. A hollow-fiber solution-spinning system. The fiber is spun into a coagulation bath, where the polymer spinning solution precipitates forming the fiber. The fiber is then washed, dried, and taken up on a roll.

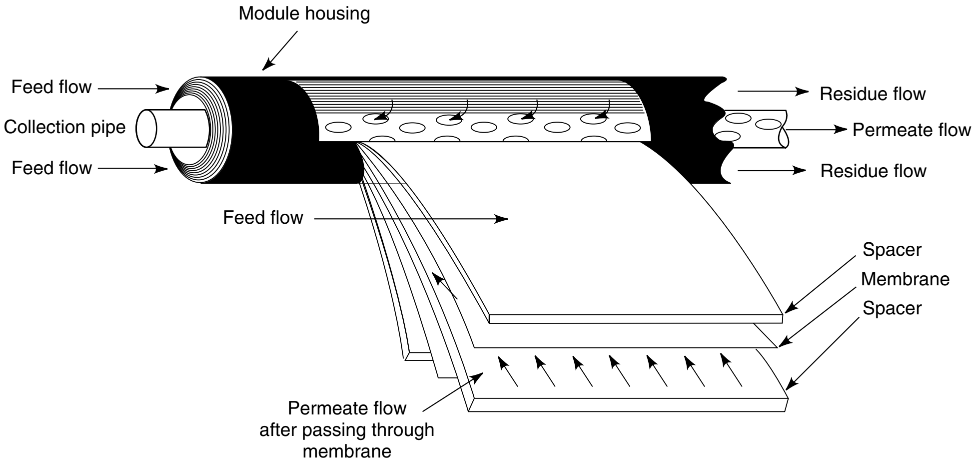


Fig. 18. Spiral-wound membrane module.

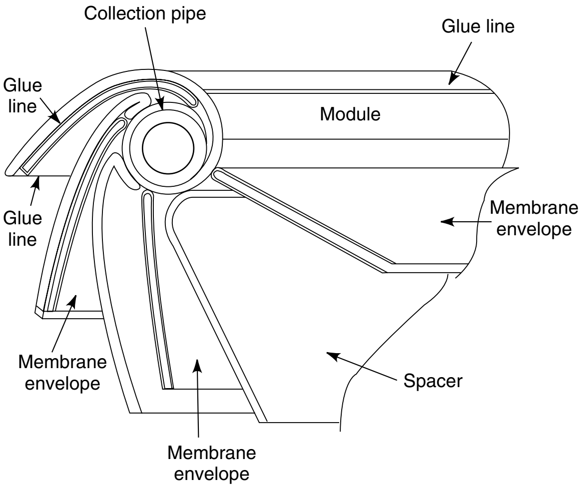


Fig. 19. Multileaf spiral-wound module, used to avoid excessive pressure drops on the permeate side of the membrane. Large, 30-cm diameter modules may have as many as 30 membrane envelopes, each with a membrane area of about 2 m^2.

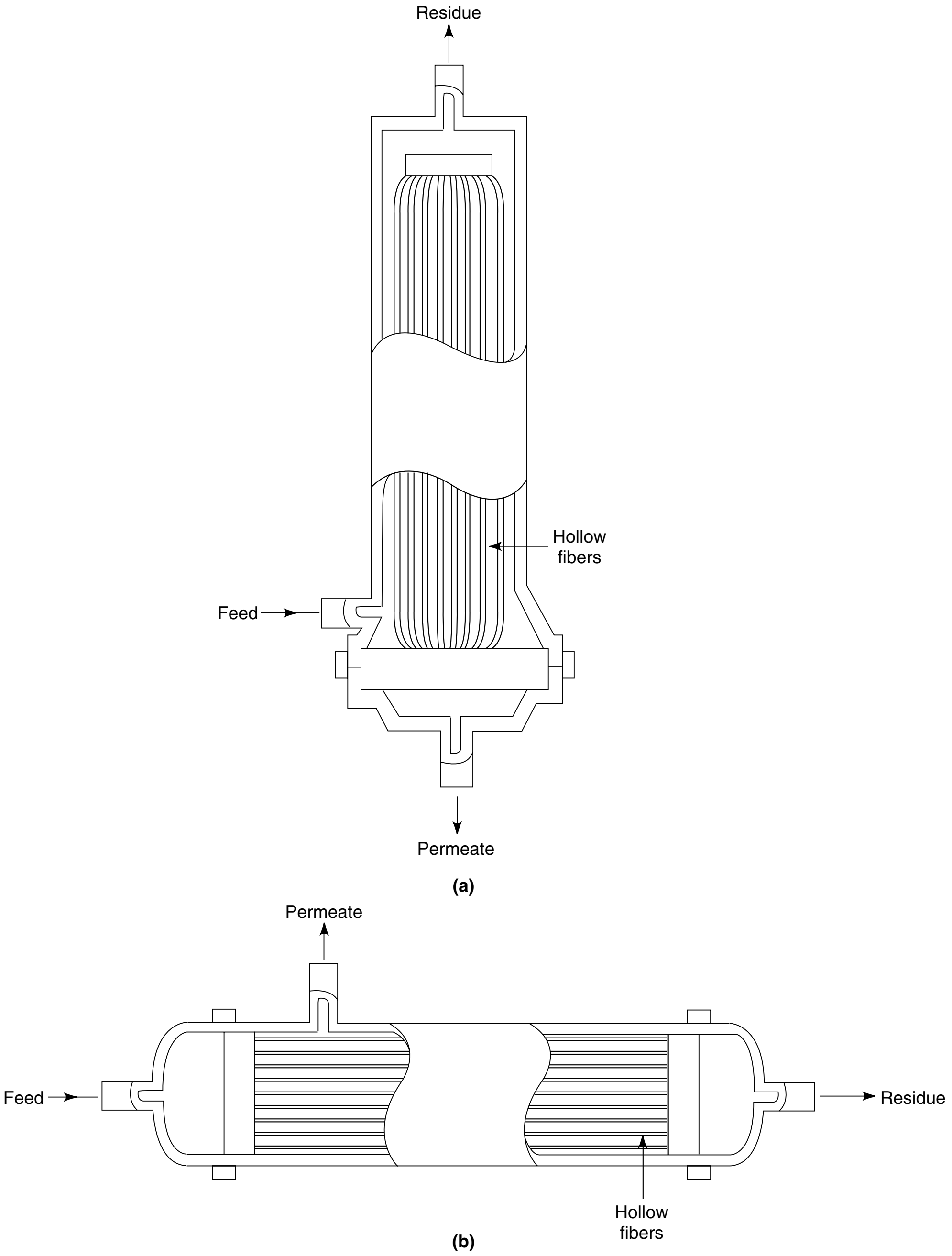
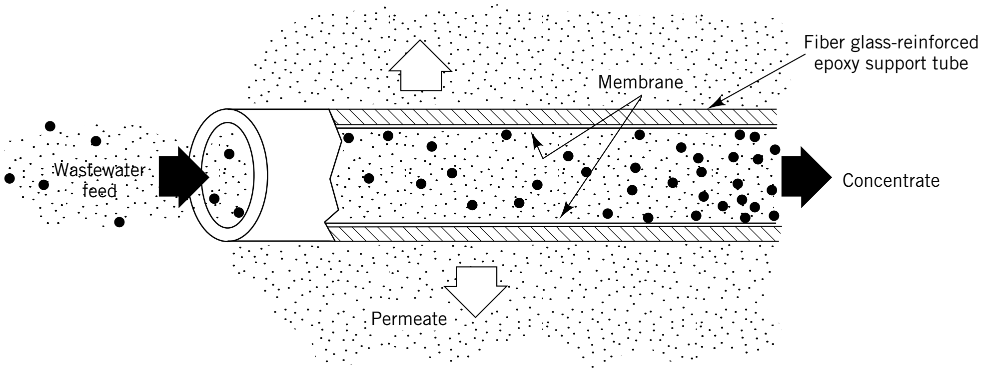


Fig. 20. Two types of hollow-fiber modules used for gas separation, reverse osmosis, and ultrafiltration applications. (**a**) Shell-side feed modules are generally used for high pressure applications up to ~7 MPa (1000 psig). Fouling on the feed side of the membrane can be a problem with this design, and pretreatment of the feed stream to remove particulates is required. (**b**) Bore-side feed modules are generally used for medium pressure feed streams up to ~1 MPs (150 psig), where good flow control to minimize fouling and concentration polarization on the feed side of the membrane is desired.



(a)

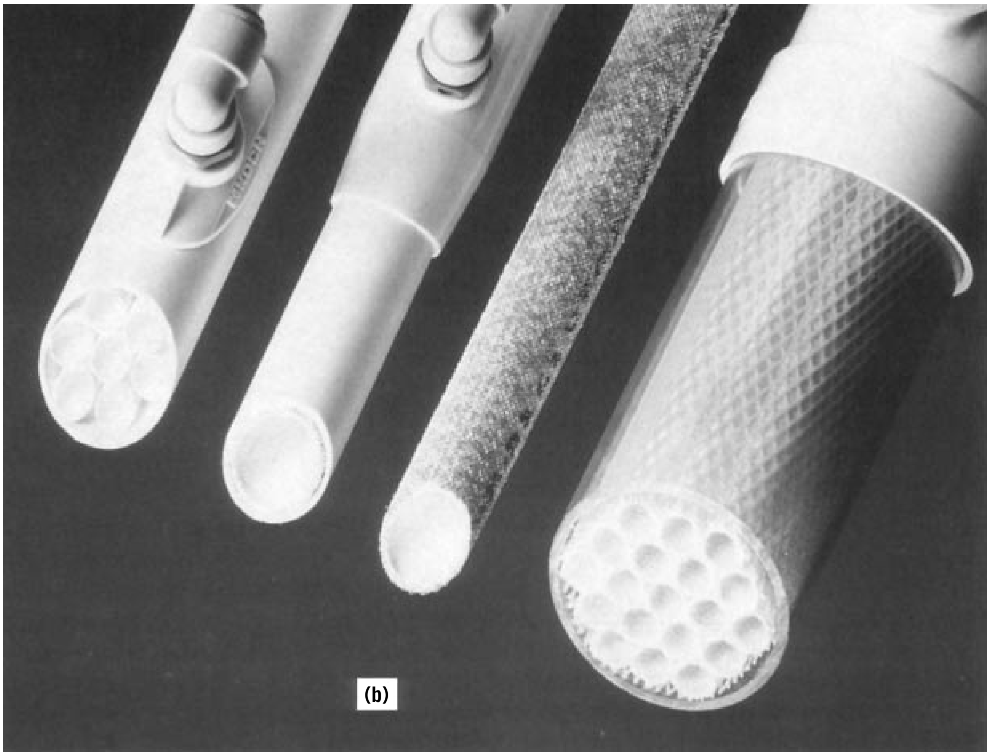


Fig. 21. (**a**) Typical tubular ultrafiltration module design. In the past, modules in the form of 2–3 cm diameter tubes were common; more recently, 0.5–1.0 cm diameter tubes, nested inside a simple pipe (**b**), have been introduced. (Courtesy of Koch Membrane Systems, Inc.)

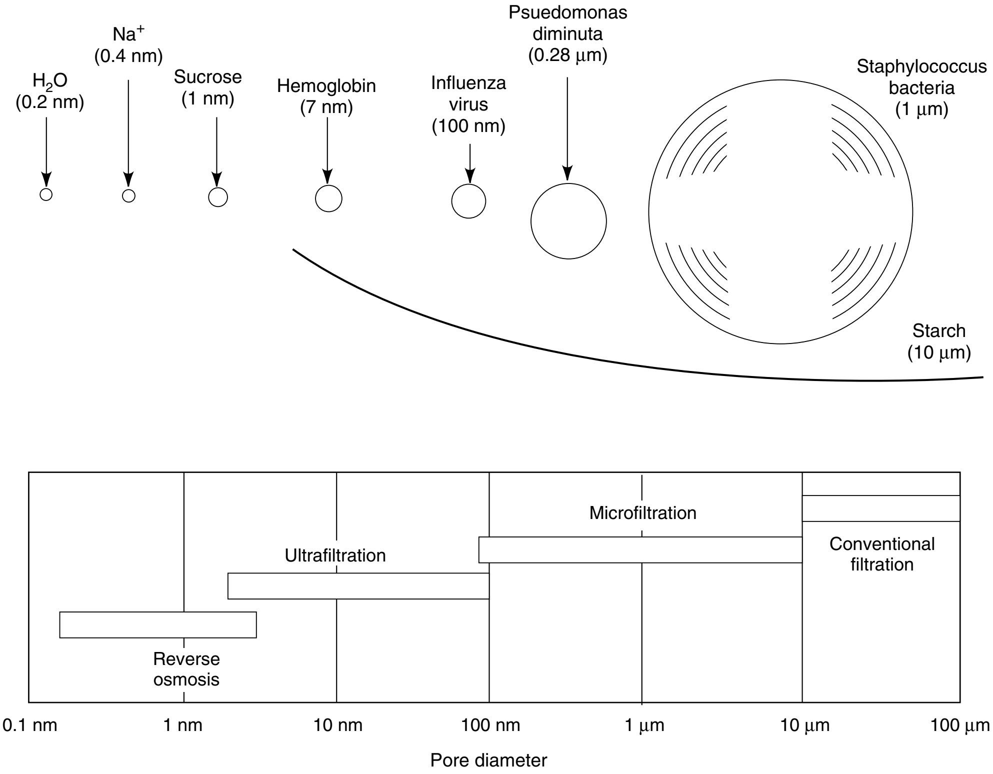
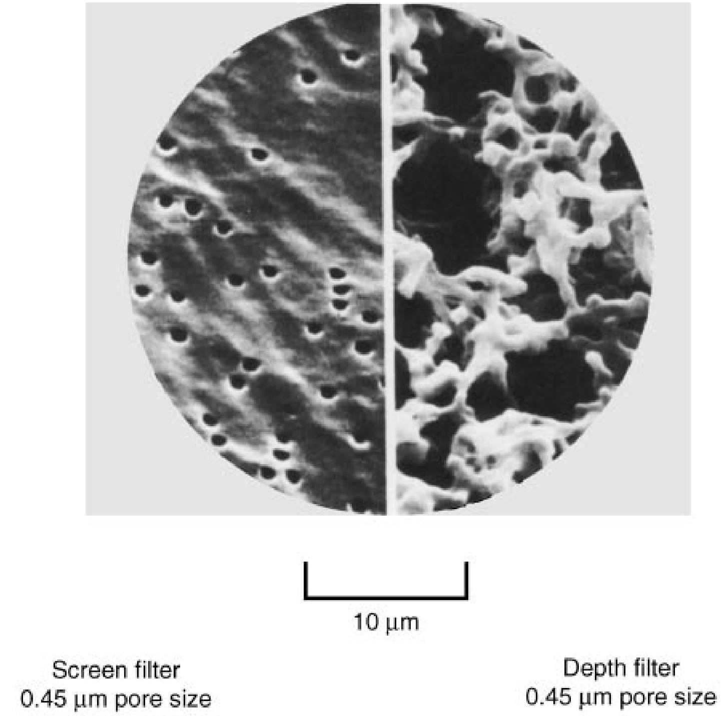


Fig. 22. Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic.



Cross- Sectional Comparision

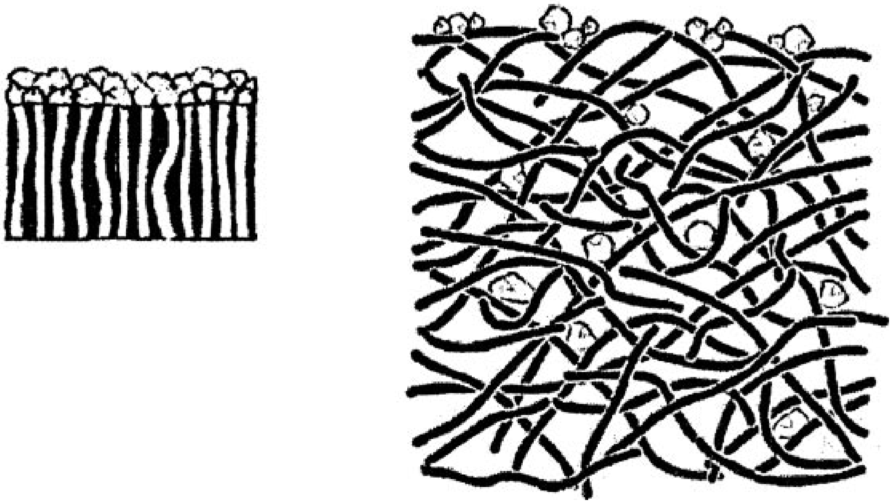


Fig. 23. Surface scanning electron micrograph and schematic comparison of nominal 0.45-mm screen and depth filters. The screen filter pores are uniform and small and capture the retained particles on the membrane surface. The depth filter pores are almost 5–10 times larger than the screen filter equivalent. A few large particles are captured on the surface of the membrane, but most are captured by adsorption in the membrane interior.

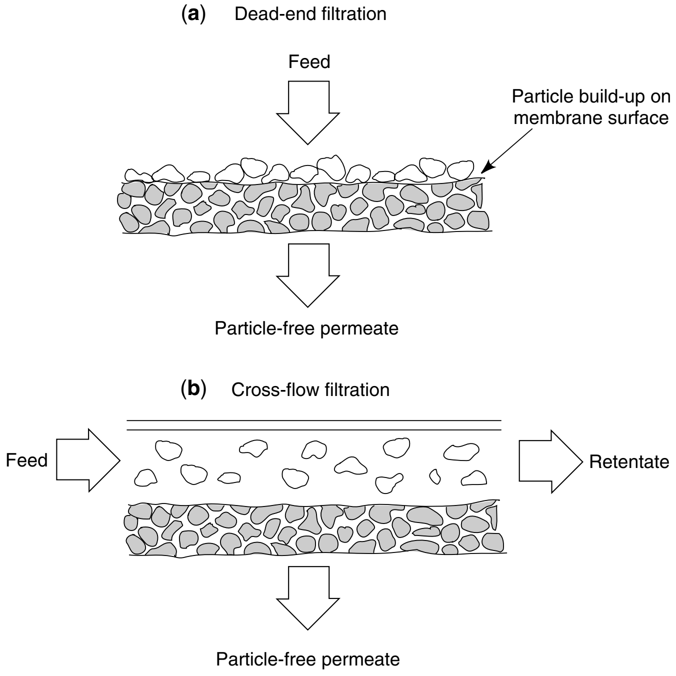


Fig. 24. Schematic representation of dead-end and cross-flow filtration with microfiltration membranes. The equipment used in dead-end filtration is simple, but retained particles plug the membranes rapidly. The equipment required for cross-flow filtration is more complex, but the membrane lifetime is longer.

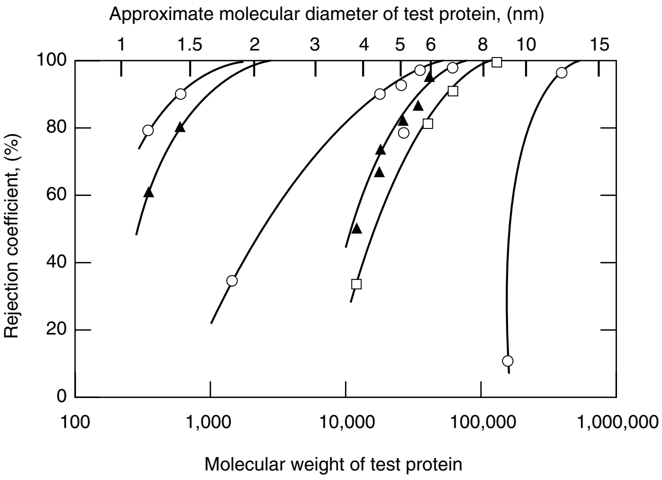


Fig. 25. Rejection of test proteins as a function of molecular weight, in a series of ultrafiltration membranes with different molecular weight cutoffs. As these data show, membranes with complete sharp molecular weight are not found outside of manufacturers' catalogs.

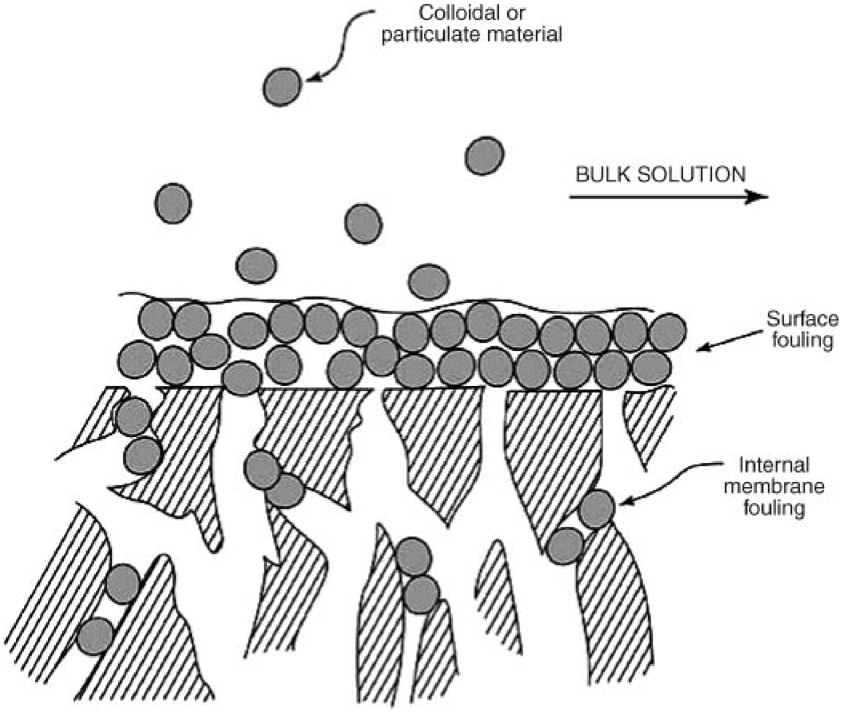


Fig. 26. Schematic representation of fouling on an ultrafiltration membrane. *Surface fouling* is the deposition of solid material on the membrane that consolidates over time. This fouling layer can be controlled by high turbulence, regular cleaning, and using hydrophilic or charged membranes to minimize adhesion to the membrane surface. Surface fouling is generally reversible. *Internal fouling* is caused by penetration of solid material into the membrane, which results in plugging of the pores. Internal membrane fouling is generally irreversible.

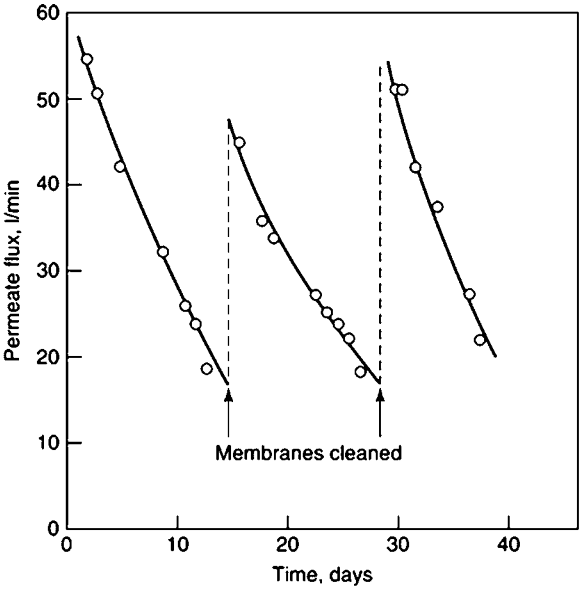


Fig. 27. Ultrafiltration flux as a function of time of an electrocoat paint latex solution. Because of fouling, the flux declines over a period of days. Periodic cleaning is required to maintain high fluxes.

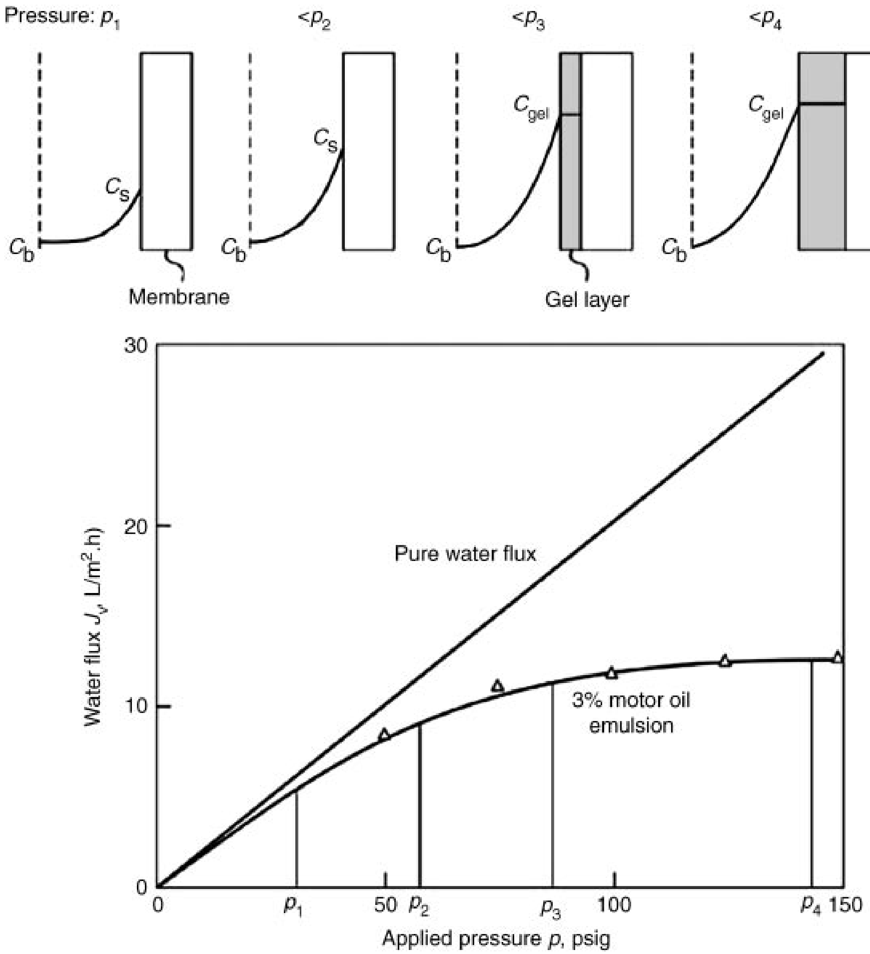


Fig. 28. The effect of pressure on ultrafiltration membrane flux and the formation of a secondary gel layer. Ultrafiltration membranes are best operated at pressures between p_2 and p_3 at which the gel layer is thin. Operation at high pressures such as p_4 leads to formation of thick gel layers, which can consolidate over time, resulting in permanent fouling of the membrane.

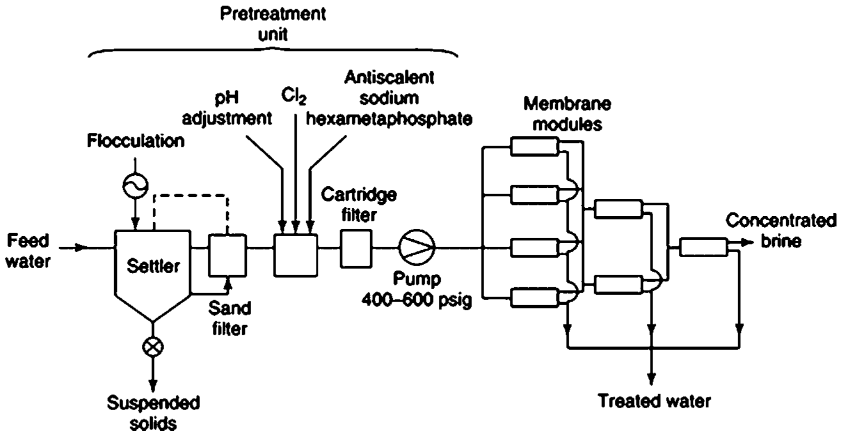


Fig. 29. Flow schematic of a typical brackish water reverse osmosis plant. The plant contains seven pressure vessels, each containing six membrane modules. The pressure vessels are in a "Christmas tree" array to maintain a high feed velocity through the modules.

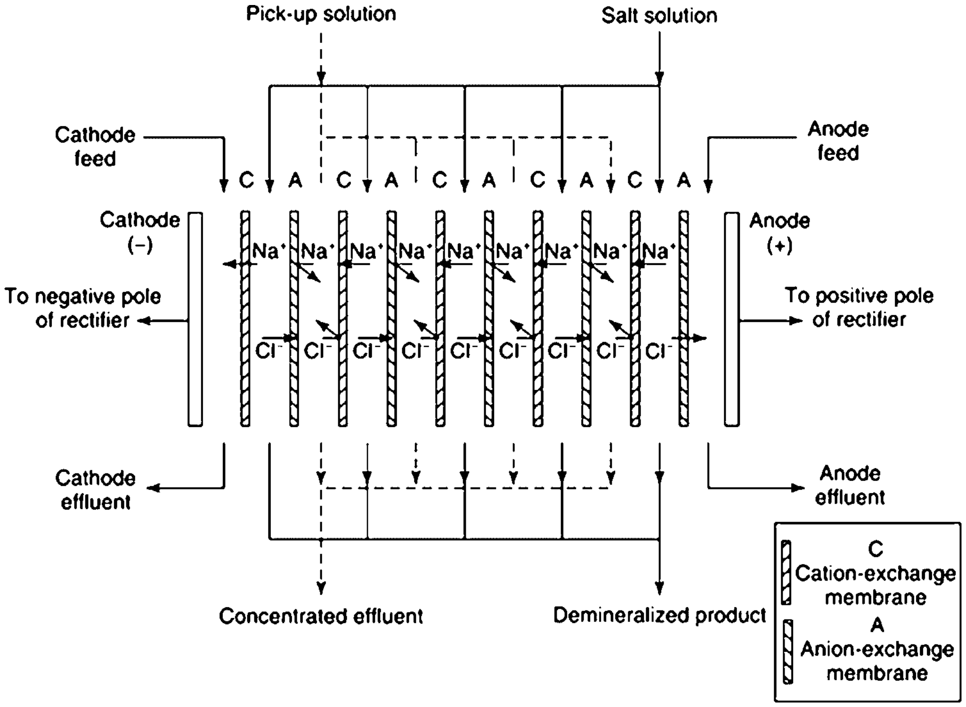


Fig. 30. Schematic diagram of a plate-and-frame electrodialysis stack. Alternating cation and anion permeable membranes are arranged in a stack of up to 100 cell pairs: C, cation-exchange membrane; A, anion-exchange membrane.

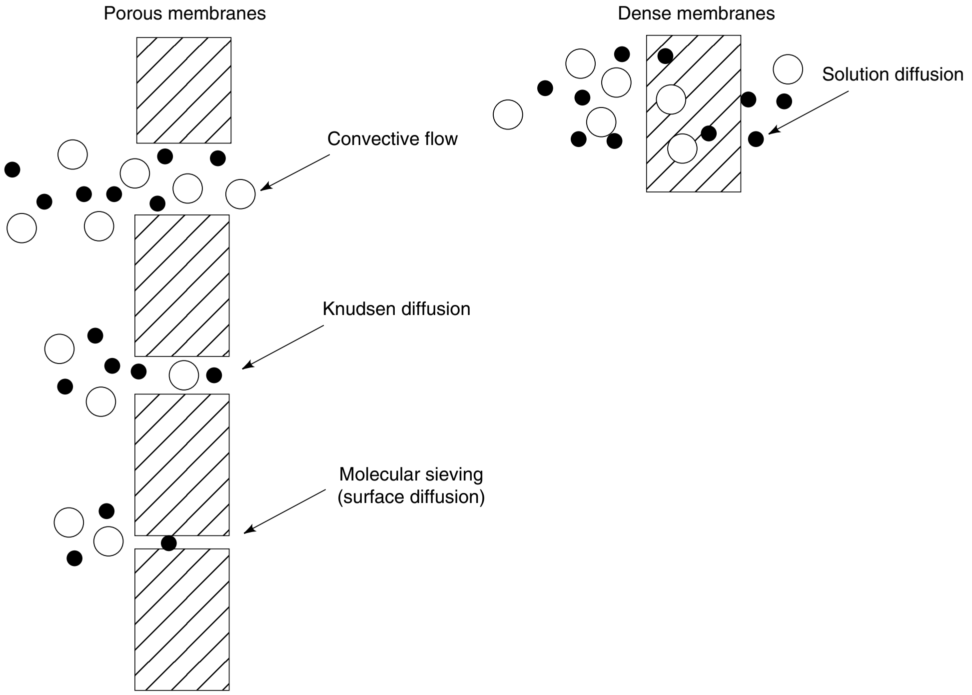


Fig. 31. Mechanisms for permeation of gases through porous and dense gas separation membranes.

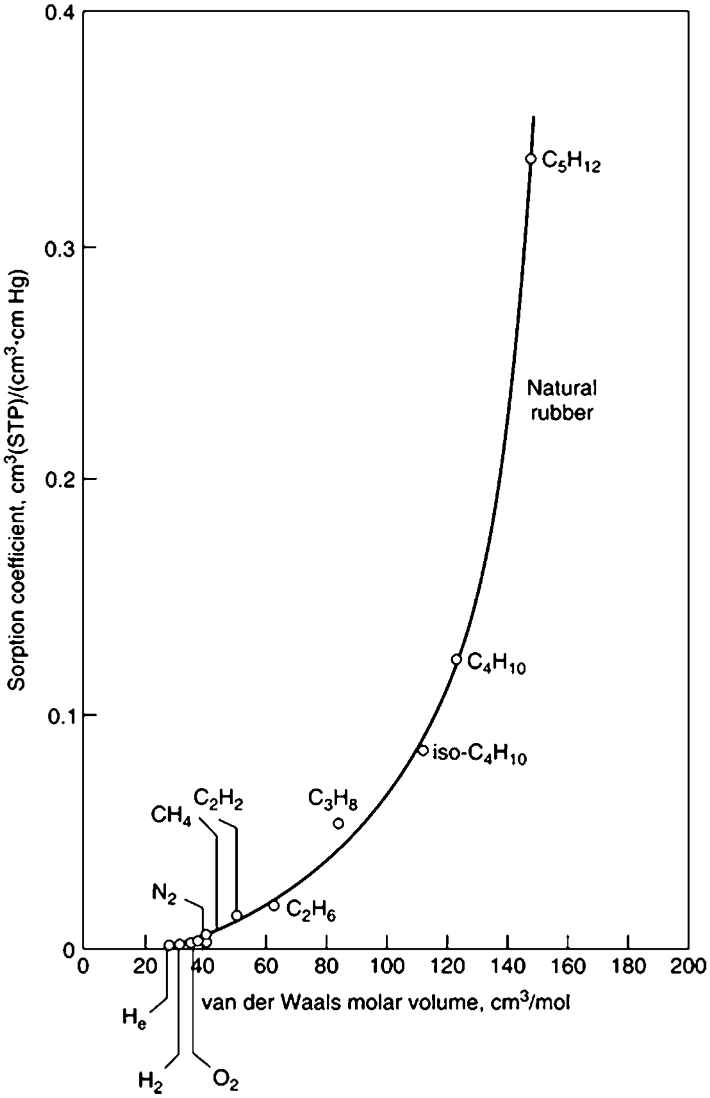


Fig. 32. Gas sorption coefficient as a function of molar volume for natural rubber membranes. Larger permeants are more condensable and have higher sorption coefficients.

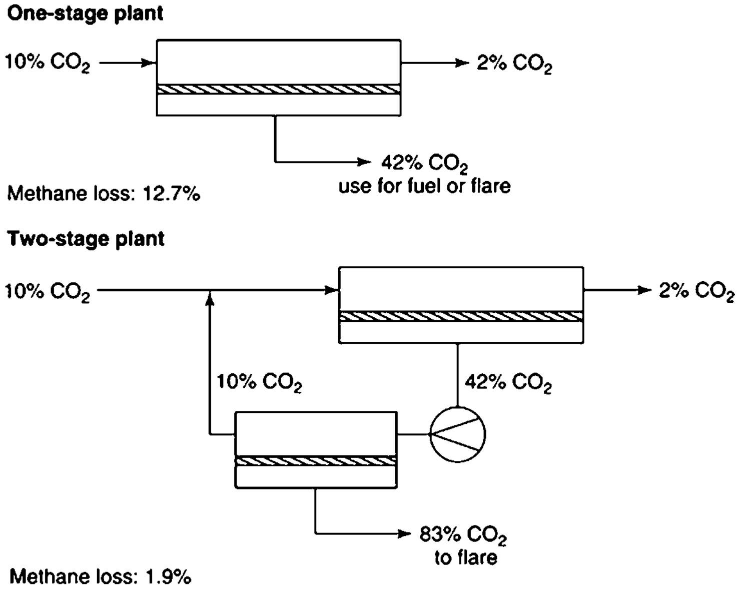


Fig. 33. Flow scheme of one-stage and two-stage membrane separation plants to remove carbon dioxide from natural gas (α_{CO_2}/CH_4 of 15 is typical for cellulose acetate membranes). Because the one-stage design has no moving parts, it is very competitive with other technologies especially if there is a use for the low pressure permeate gas. Two-stage processes are more expensive because a large compressor is required to compress the permeate gas. However, the loss of methane with the fuel gas is much reduced.

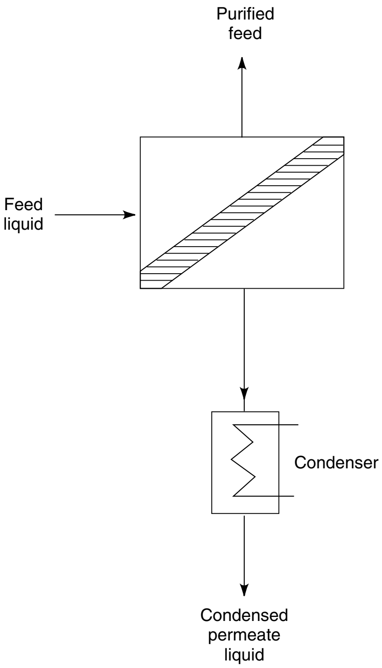


Fig. 34. Schematic of the basic pervaporation process.

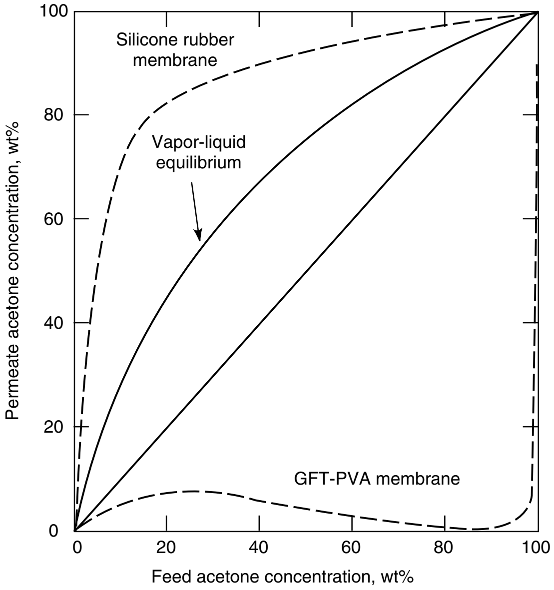


Fig. 35. The pervaporation separation of acetone–water mixtures achieved with a water-selective PVA membrane and with an acetone-selective silicone rubber membrane. The PVA membrane is best suited to removing small amounts of water from a concentrated acetone solution, whereas the silicone rubber membrane is best suited to removing small amounts of acetone from a dilute acetone stream. Reprinted from Ref. 1986 by courtesy of Marcel Dekker, Inc.

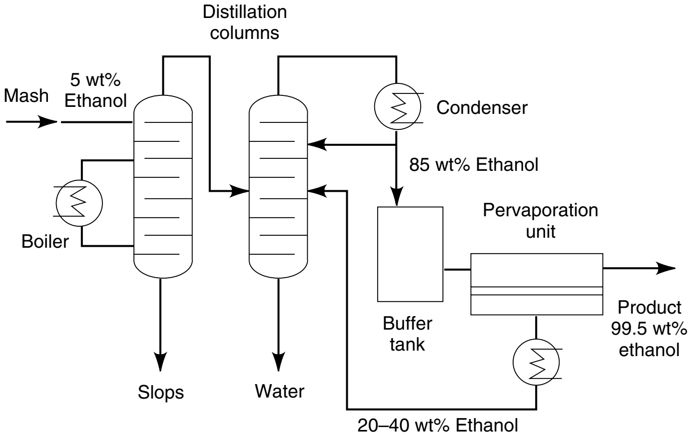


Fig. 36. Integrated distillation/pervaporation plant for ethanol recovery from fermentors. The distillation columns concentrate the ethanol/water mixture from 5 to 80%. The pervaporation membrane produces a 99.5% ethanol product stream and a 40–50% ethanol stream that is sent back to the distillation column.

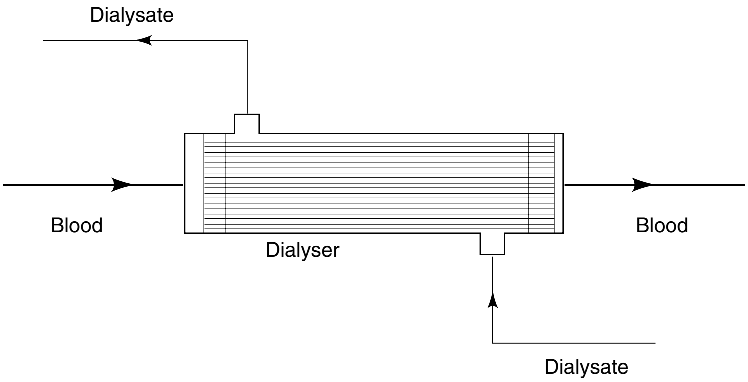


Fig. 37. Schematic of a hollow fiber artificial kidney dialyser used to remove urea and other toxic metabolites from blood. Several million of these devices are used every year.

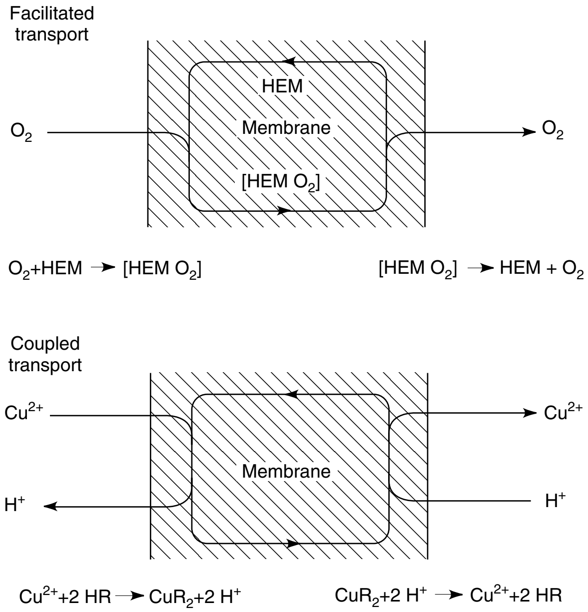


Fig. 38. Schematic examples of facilitated transport of gases and metal ions. The gas-transport example shows the transport of oxygen across a membrane using hemoglobin (HEM) as the carrier agent. The ion-transport example shows the transport of copper ions across the membrane using a liquid ion-exchange reagent as the carrier agent.

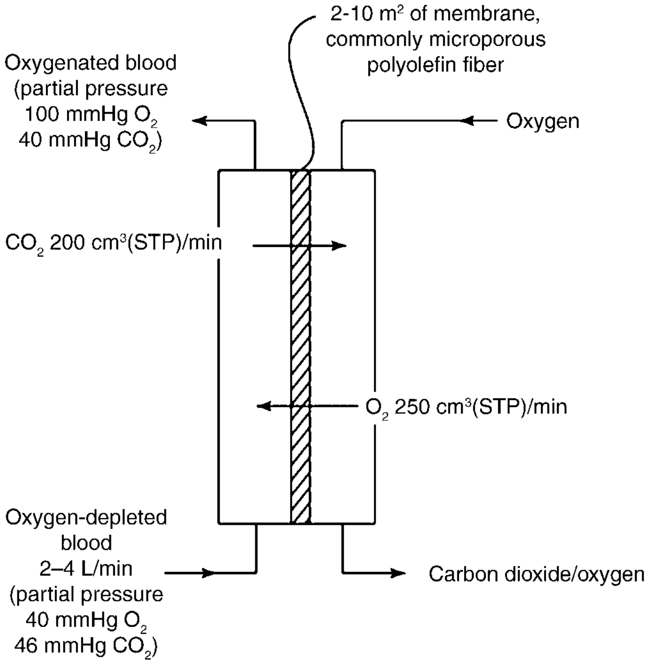


Fig. 39. Flow schematic of a membrane blood oxygenator. The device is designed to deliver about 250 cm^3(STP)/min of oxygen to the blood and remove about 200 cm^3(STP)/min of carbon dioxide from the blood.

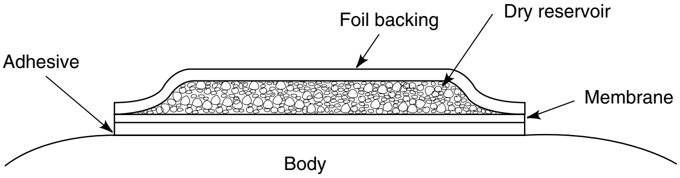


Fig. 40. Schematic of transdermal patch in which the rate of delivery of drug to the body is controlled by a polymer membrane. Such patches are used to deliver many drugs including nitroglycerine, estradiol and nicotine.

Table 1. **Less Widely Used Membrane Preparation Techniques**

Preparation technique	Membrane characteristics	References
plasma polymerization	monomer is plasma polymerized onto the surface of a support film; resulting chemistry is complex	(38–41)
reactive surface treatment	an existing membrane is treated with a reactive gas of monomer to form an ultrathin surface layer	(42–44)
dynamically formed membranes	a colloidal material is added to the feed solution of an ultrafiltration membrane; a gel forms on the membrane surface and enhances the membrane selectivity	(45,46)
molecular sieve membranes	an ultrafine microporous membrane is formed from a dense, hollow-fiber poly-meric membrane by carbonizing or from a glass hollow fiber by chemical leaching; pores in the range 0.5−2 nm are claimed	(47–50)
microporous metal membranes by electrochemical etching	aluminum metal, for example, is electrochemically etched to form a porous aluminum oxide film; membranes are brittle but uniform with small pore size 0.02−2.0 μm	(51,52)

Table 2. **Characteristics of Module Designs**

Property	Hollow-fine fibers	Capillary fibers	Spiral-wound	Plate and frame	Tubular
manufacturing cost, \$/m^2	5–20	20–100	30–100	100–200	50–200
resistance to fouling	very poor	good	moderate	good	very good
parasitic pressure drop	high	moderate	moderate	low	low
suitability for high pressure operation	yes	no	yes	can be done with difficulty	can be done with difficulty
limitation to specific types of membrane	yes	yes	no	no	no

Table 3. **Various Membrane Separation Technologies**

	Process	Status
developed technologies	microfiltration ultrafiltration reverse osmosis electrodialysis	well-established unit processes; no major breakthroughs seem imminent
developing technologies	gas separation pervaporation	a number of plants have been installed; market size and number of applications served are expanding rapidly
to-be-developed technologies	facilitated transport	major problems remain to be solved before industrial systems will be installed on a large scale

Table 4. **Status of Membrane Gas Separation Processes**[a]

Process	Application	Comments
	Established processes	
oxygen/nitrogen	nitrogen from air	processes are all well developed, only incremental improvements in performance expected
hydrogen/methane; hydrogen/nitrogen; hydrogen/carbon monoxide	hydrogen recovery; ammonia plants and refineries	
water/air	drying compressed air	
	Developing processes	
VOC/air	air pollution control applications	several applications being developed, significant growth expected as the process becomes accepted
light hydrocarbons from nitrogen or hydrogen	reactor purge gas, petrochemical process streams, refinery waste gas	application is expanding rapidly
carbon dioxide/methane	carbon dioxide from natural gas	many plants installed but better membranes are required to change market economics significantly
	To-be-developed processes	
C_{3+} hydrocarbons/ methane	NGL recovery from natural gas	field trails and demonstration system tests under way, potential market is large
hydrogen sulfide, water/methane	natural gas treatment	niche applications, difficult for membranes to compete with existing technology
oxygen/nitrogen	oxygen enriched air	requires better membranes to become commercial, size of ultimate market will depend on properties of membranes developed, could be very large
organic vapor mixtures	separation of organic mixtures in refineries and petrochemical plants	requires better membranes and modules, potential size of application is large

[a] From Ref. 68.