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Overview of Membrane Science and Technology

Membrane Technology and Applications, Fourth Edition. Richard W. Baker.

1.1 Introduction

In the last 50 years, synthetic membranes have changed our lives. Two million people worldwide are kept alive by hemodialysis, 10 trillion gallons of drinking water are produced annually by reverse osmosis (also sometimes known as RO), and there has been a revolution in municipal sewage treatment thanks to modern microfiltration and ultrafiltration systems. Transdermal patches can help you quit smoking, and avoid getting seasick or pregnant. Membranes are on the brink of being able to capture 90% of the carbon dioxide emitted by power plants. Membranes have become big business.

The key property of a membrane is that it has limited permeability. A membrane is simply a barrier through which different chemical species pass at different rates. In controlled drug delivery, this mechanism is used to moderate the rate at which a drug is dispensed from a reservoir to the body. In industrial applications, the membrane is chosen such that one component of a mixture permeates much faster than another, allowing separation of the components.

This book provides a general introduction to membrane science and technology. Chapters 2–5 cover membrane science, that is, topics that are basic to all membrane processes, such as transport mechanisms, membrane preparation, and boundary layer effects. The next six chapters cover the industrial membrane separation processes that represent the heart of current membrane technology. Carrier transport is covered next, followed by a chapter on membrane contactors and one reviewing the medical applications of membranes. The book closes with a chapter that describes some intriguing membranes and processes that are worthy of inclusion by virtue of their technical ingenuity and level of ongoing research, although they may never make it to the big leagues.

Chapters 2 and 3 on the theory of membrane permeation are not an easy read. The chapter on the solution-diffusion model has more than 100 equations. Readers interested in membrane technology as a unit operation can skip these theory chapters and move directly to the process chapters. Each of these starts with a short theoretical introduction and the basic equations, and then it is on to process design and applications. Readers who are using the book as an introduction to research careers will find the theory chapters of more interest.

1.2 Historical Development of Membranes

Systematic studies of membrane phenomena can be traced to the eighteenth-century philosopher scientists. In 1748, Abbé Nolet, better known for his work on electricity, but a man of many interests, coined the word ‘osmosis’ to describe permeation of water through a diaphragm. 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 membrane investigators experimented with every 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 early workers improved on Bechhold’s technique, and by the early 1930s microporous nitrocellulose membranes were commercially available for

laboratory use. During the next 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate.

Membranes found their first substantial application in the testing of drinking water at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down, and laboratory filters to test for water safety were needed urgently. The research effort to develop these filters, sponsored by the US Army, was later exploited by the Millipore Corporation, the first and still the largest US microfiltration membrane producer.

By 1960, the elements of modern membrane science had been developed, but membranes were used only in laboratories and for a few small, specialized industrial applications. No significant membrane industry existed, and total annual sales probably did not exceed US$20 million in today's dollars. Membranes suffered from four problems that prohibited their widespread use: they were too unreliable, too slow, too unselective, and too expensive. Solutions to each of these problems have been developed, and membrane-based separation processes are now 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 membranes [2]. These membranes were, and still are, made from a polymer solution by a casting process that produces a structure that is asymmetric or anisotropic (both words are commonly used) in cross section. The membrane consists of an ultrathin, selective surface film, which performs the separation, supported on a much thicker but much more permeable microporous layer, which provides the mechanical strength. The process Loeb and Sourirajan were interested in was reverse osmosis, a way to make drinking water from salt water by permeating the water and retaining the salt. Because the selective layer was so thin, the flux of the first Loeb–Sourirajan membrane was 20 times higher than that of any membrane then available and made RO a feasible method of desalting water. The work of Loeb and Sourirajan, and the timely infusion of large sums of research and development dollars from the US Department of Interior, Office of Saline Water (OSW), resulted in the commercialization of reverse osmosis.

Concurrent with the development of industrial applications was the independent development of membranes for medical separation processes, in particular, the artificial kidney. Kolff and Berk [3] had demonstrated the first successful artificial kidney in the Netherlands in 1943. Their device consisted of a coil of cellophane membrane through which the patient's blood was pumped, while a solution of isotonic saline circulated on the other side. Toxic components permeated from the blood to the saline solution. It took almost 20 years to refine the technology for use on a large scale, but these developments were complete by the early 1960s. Since then, the use of membranes in artificial organs has become a major life-saving procedure. About two million people are now sustained by artificial kidneys. A further million undergo open-heart surgery each year, a procedure made possible by the membrane blood oxygenator, in which carbon dioxide in the patient's blood is removed and replaced with oxygen, a task normally performed by the lungs. The sales of these medical devices exceed the total industrial membrane separation market.

The creation of the modern membrane industry can be divided into the four phases shown in Figure 1.1. In the first phase, building on the original Loeb–Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed. Using these processes, high-performance membranes with selective surface layers as thin as 0.1 μm or less are now produced commercially by many companies. Methods of packaging membranes into large-membrane-area spiral-wound, hollow fine fiber, capillary, and plate-and-frame modules were also developed, and advances were made in improving membrane stability. The support of the OSW was key to these developments.

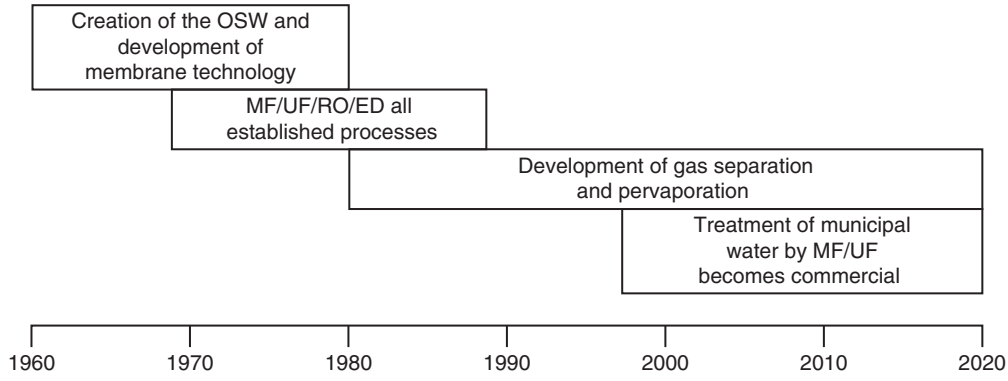

Figure 1.1 *The development of the membrane separation industry, 1960–2020.*

In the second phase, beginning in the early 1970s, the developments that came out of the OSW program began to appear in commercial membrane units; by the 1980s microfiltration (to remove bacteria and viruses from water), ultrafiltration (to separate proteins and other dissolved macromolecules), and reverse osmosis and electrodialysis (both for desalting water) were all established processes.

The third phase, which began in the 1980s, was the emergence of industrial gas separation processes. The first major product was the Monsanto Prism® membrane for hydrogen separation, introduced in 1980 [4]. 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 natural gas. Gas separation technology is continuing to evolve and expand; further growth will be seen in the coming years.

The final development phase, which began in earnest in the late 1980s and came to fruition in the mid-1990s, was the development of ultrafiltration systems for the treatment of municipal drinking water and municipal sewage. These applications had been targets for membrane developers for more than 20 years, but their commercialization was impeded by low fluxes, caused by intractable membrane fouling. In the late 1980s, Dr. Kazuo Yamamoto began to develop low-pressure, submerged, air-sparged membranes [5]. It took another 10 years for companies like Kubota, Mitsubishi Rayon, and Zenon to bring this breakthrough concept to the commercial stage, but by the late 1990s, systems with effective fouling control began to be installed. Since then, treatment of municipal water has become one of the most rapidly growing areas of membrane technology. Membrane systems are cost competitive with conventional biological treatment and produce a far superior treated water product. Membrane plants that contain more than one million square meters (250 acres) of membrane, and able to treat the wastewater from a city, are in operation.

1.3 Membrane Transport Theory

The most important practical property of membranes is their ability to sort sheep from goats. In other words, they can discriminate between closely related species. Throughout the twentieth century, two models – the pore-flow model and the solution-diffusion model – were used to describe the mechanisms of permeation. These models are illustrated in Figure 1.2a, b. Over

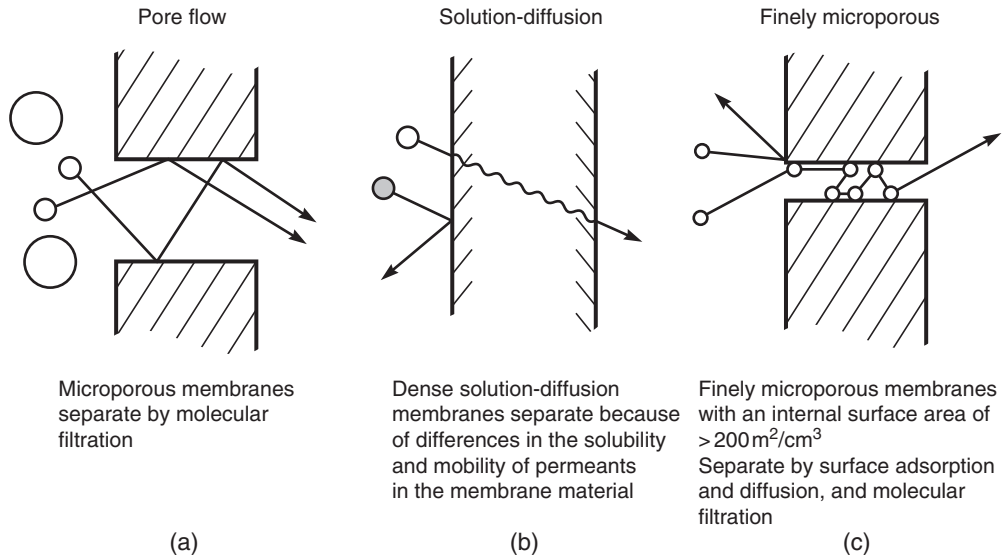

Figure 1.2 *In traditional membranes, molecular transport can be described by a flow through permanent pores (as in (a), for porous membranes), or by the solution-diffusion mechanism (as in (b) for dense membranes). Classes of very finely microporous membranes also exist, as shown in (c). In such membranes, the mechanism of permeation is complex, conforming to neither model.*

the last 20 years, membranes with extremely fine pores, some as small as 5 Å in diameter, have been developed; their mechanism of permeation is complicated and conforms to neither traditional model. These membranes are shown in Figure 1.2c.

According to the pore-flow model of Figure 1.2a, permeants are transported by flow through tiny pores. The flow is convective and occurs because a driving force, usually a pressure gradient, exists between the feed and permeate sides of the membrane. Separation occurs by filtration, that is, the selective retention on the feed side of species that are too large to pass through the pores. Care must be taken in characterizing pore size because most pores are not the perpendicular, straight cylinders shown in the figure, nor are they uniform in size. Nevertheless, this familiar model describes permeation in ultrafiltration and microfiltration processes, where the membrane pores are more than 20 Å in diameter.

The solution-diffusion model, Figure 1.2b, describes transport in membranes that lack permanent pores. In this case, permeants dissolve in the membrane material as in a liquid, and then diffuse through the membrane down a concentration gradient. Transport depends both on the solubility of the permeant in the polymer of which the membrane is made and the diffusion rate once dissolved. Depending on the polymer and the permeant, either solution or diffusion may be the dominant controlling phenomenon. The product of these terms, known as the permeability, is characteristic for a given permeant, and permeants are separated because of differences in their permeabilities. The solution-diffusion model, once controversial, has a secure mathematical basis and is now firmly accepted as describing permeation through the dense polymer membranes used in dialysis, gas separation, reverse osmosis, and pervaporation.

Work in the last 20 years has given rise to a spectrum of finely microporous membrane types that fall between the clearly nonporous solution-diffusion membranes of Figure 1.2b and the clearly microporous filtration membranes of Figure 1.2a. Shown in Figure 1.2c, these intermediate types, which may be made from a variety of materials, including zeolites, metal/organic hybrids, and carbonized polymers, are characterized by pores of diameter in the 5–25 Å range. These pores may change in size and shape over extended periods of time, but in the time frame of permeation, they are permanent.

Because the pores are so small, the ratio of the pore surface area to the pore volume is very large, typically of the order 100–1000 m^2/cm^3 of membrane material. Transport through these membranes is controlled not only by molecular sieving, as in ultrafiltration, but also by adsorption effects on the huge internal surface area of the pore walls; modeling of their transport behavior is more complicated, therefore, than for either of the traditional membrane types. Though their transport properties defy a simple theoretical model, these very finely microporous materials can manifest exceptional permeances and selectivities and are the subject of much current research.

1.4 Types of Membranes

This book is limited to synthetic membranes, excluding all biological structures, but 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 nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it. A normal filter meets this definition of a membrane, but, by convention, the term filter is usually used for structures that retain particles larger than about 1–10 μm in diameter. A polymeric membrane may be referred to as isotropic or symmetrical, terms that are used interchangeably for membranes that are homogeneous (uniform in composition and structure). In the alternative, it may be anisotropic or asymmetric, that is, chemically or physically heterogeneous (containing holes or pores of varying dimensions or consisting of some form of layered structure). Other special types of membrane that may themselves be isotropic or anisotropic, but that are generally referred to by their distinguishing characteristic, include charged membranes, supported liquid membranes, and mixed matrix membranes. The principal types of membrane are shown schematically in Figures 1.3–1.5 and are described briefly below.

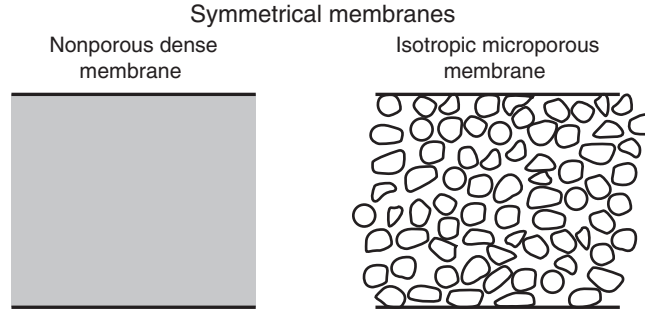

Figure 1.3 *Isotropic membranes. The membrane may be microporous or dense but has a uniform structure throughout.*

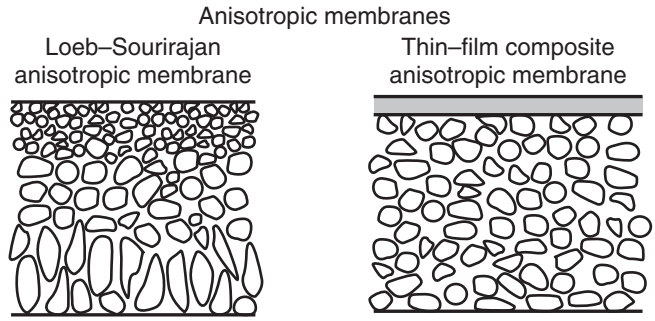

Figure 1.4 *Anisotropic membranes, characterized by a relatively open support structure underlying the selective layer.*

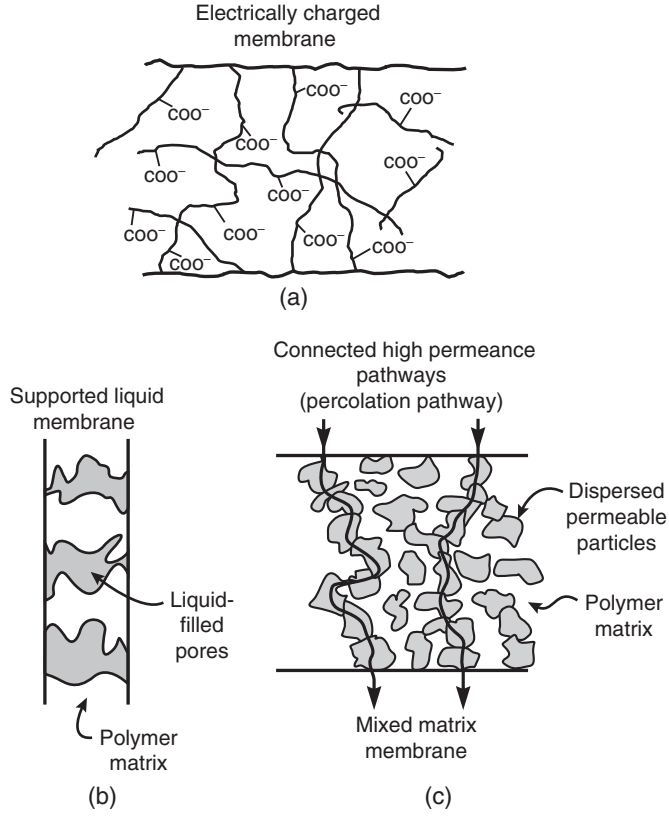

Figure 1.5 *Membranes with special features: (a) an electrically charged membrane; (b) a supported liquid membrane; and (c) a mixed matrix membrane.*

1.4.1 Isotropic Membranes

1.4.1.1 Nonporous, Dense Films

Nonporous, dense polymer films transport permeants by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. There are no permanent pores; the separation of various components of a mixture is related to their relative transport rate within the polymer material, which is determined by a combination of their diffusivity and solubility. Thus, nonporous, dense membranes can separate permeants of similar size (and hence diffusivity) if the permeant concentrations in the membrane material (that is, their solubilities in the polymer) differ significantly. On the other hand, if the permeants have similar solubilities but differ in size, diffusion determines the separation that can be achieved, because small molecules diffuse faster than big ones.

Unsupported dense films of the type shown in Figure 1.3 need to be at least a few tens of microns thick to have any mechanical strength at all. Hence their fluxes are generally much too low for cost-effective industrial separations. They are used for research purposes to determine the intrinsic permeation properties of polymer materials and as drug delivery mediators in transdermal devices.

1.4.1.2 Microporous Membranes

A microporous isotropic membrane is similar in structure and function to a conventional filter. It has a rigid, highly voided structure with interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01–10 μm in diameter. All particles larger than the pore diameter are completely rejected by the membrane. Particles smaller than the pore diameter can enter the membrane but may then be captured by adsorption onto the pore walls or entanglement at pore constrictions in the interior of the membrane. As a result, microporous membranes can be impermeable to particles much smaller than their geometric pore diameter would suggest. For this reason, microporous membranes are generally characterized by their *effective* pore diameter, that is, the size of the smallest particle that is completely retained by the membrane. This type of isotropic membrane is mostly used for microfiltration.

1.4.2 Anisotropic Membranes

The transport rate of a species through a membrane is inversely proportional to the membrane thickness; the thicker the membrane, the lower the flux. 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 thicknesses of about 20 μm or above. The development of novel fabrication techniques to produce anisotropic membrane structures was one of the major breakthroughs of membrane technology. Anisotropic membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure, as shown in Figure 1.4. The surface layer and its substructure may be formed in a single operation, as in the Loeb–Sourirajan technique. Alternatively, a composite membrane, in which the layers are made from different polymers, can be made by forming the support membrane, then applying a very thin dense coating. In either case, the separation properties and permeation rates of the membrane are determined mainly by the surface skin or applied coating layer; the substructure offers little resistance to permeation of the species to be separated, and functions solely as a mechanical support. The advantages of the higher fluxes provided by anisotropic and composite polymer membranes are so great that almost all reverse osmosis, gas separation, pervaporation, and ultrafiltration processes use such membranes.

1.4.3 Membranes with Special Features

1.4.3.1 Electrically Charged Membranes

Electrically charged membranes can be dense or microporous, but are most commonly very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positive ions is referred to as an anion exchange membrane, because it attracts and transports negatively charged anions from the surrounding fluid. Similarly, a membrane containing fixed negative 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. The separation is affected by the charge and concentration of the ions in solution. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis.

1.4.3.2 Mixed Matrix Membranes

In recent years, a great deal of work has been spent on mixed matrix membranes. These membranes consist of a dispersed phase of selective, highly permeable fine particles, for example zeolite particles, in a polymer matrix that holds everything together. The idea is to combine the selectivity of the molecular level pores in the zeolite particles with the ease of fabrication and stability of polymeric membranes. When the volume fraction of zeolite particles in the polymer is above about 30%, there is enough particle-to-particle contact to form a continuous pathway through the zeolite phase of the membrane; this is called its percolation threshold. Despite many years of research, problems with stability and difficulty of scale-up have kept mixed matrix membranes in the laboratory.

1.4.3.3 Supported Liquid Membranes

Supported liquid membranes are microporous polymer membranes in which the pores are filled with a liquid. As with mixed matrix membranes, the microporous polymer structure serves simply as a scaffold; the liquid, which is constrained inside the pores by capillary forces, provides the separation capability. To do this, the liquid incorporates an agent that can bind reversibly with one of the components in the mixture to be treated, enabling that component to be transported preferentially across the membrane. Though they have been a subject of research interest for many years, these membranes remain undeveloped because of unsolved stability problems.

1.4.3.4 Ceramic and Metal Membranes

The discussion so far implies that all membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer-based. However, there has always been interest in using other materials. Dense metal membranes, particularly palladium membranes for separating hydrogen from gas mixtures, were tried out in a refinery over 60 years ago. Ceramic membranes, a special class of microporous membranes made from alumina, silica, and other refractory materials, are characterized by their exceptional chemical and heat resistance. They are used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required.

1.5 Membrane Processes

Five developed, and a number of developing and yet-to-be-developed, industrial membrane processes are discussed in this book. In addition, sections are included describing the use of membranes in medical applications such as kidney dialysis, blood oxygenation, and controlled drug delivery. The status of these processes is summarized in Table 1.1.

Table 1.1 *Membrane technologies characterized by their stage of development and use.*

Category	Process	Status
Developed industrial membrane separation technologies	– Microfiltration – Ultrafiltration – RO – Electrodialysis – Gas separation	Well-established unit operations
Developing industrial membrane separation technologies	– Pervaporation – Organic/organic (hyperfiltration) – Membrane contactors	A number of plants have been installed. Market size and number of applications are small but expanding
To-be-developed industrial membrane separation technologies	– Carrier transport – Piezodialysis – PRO, FO	Major problems remain to be solved before industrial systems will be installed on a large scale
Medical applications of membranes	– Artificial kidneys – Artificial lungs – Controlled drug delivery	Well-established processes. Still the focus of research to improve performance, for example, improving biocompatibility

The developed industrial membrane separation processes are microfiltration, ultrafiltration, reverse osmosis, electrodialysis, and gas separation. These processes are all well established, and their markets are served by a number of experienced companies.

1.5.1 Reverse Osmosis, Ultrafiltration, Microfiltration

The range of application of the three pressure-driven water separation processes – reverse osmosis, ultrafiltration, and microfiltration – is illustrated in Figure 1.6. Ultrafiltration (Chapter 7) and Microfiltration (Chapter 8) are similar in that the mode of separation includes molecular sieving through increasingly fine pores. The figure shows the distinction between the two as being determined by pore size, which is the simple conventional definition. It can be more convenient for practical purposes to differentiate the processes in terms of their modes of operation, but discussion of this is deferred until the two relevant chapters. Ultrafiltration and microfiltration membranes contain permanent pores usually ranging from 20 Å to 10 μm in diameter. Ultrafiltration membranes mostly operate by capturing the retained material on the surface of the membrane by molecular sieving or other effects. Microfiltration membranes operate by a combination of molecular sieving at the membrane surface and adsorption of particulates in the interior of the membrane. The uses of these filtration processes are extremely diverse and include preparation of pharmaceuticals, drinking water sterilization, and wastewater and sewage treatment.

The mechanism of separation by reverse osmosis (Chapter 6) is quite different from that of ultrafiltration and microfiltration. The membrane pores are so small, from 3 to 5 Å in diameter, that they are within the range of thermal motion of the polymer chains that form the membrane. This means there are no permanent pores in a reverse osmosis membrane, and the accepted mechanism of permeant transport is the solution-diffusion model. According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubilities and mobilities of different solutes in the membrane. The major applications of reverse osmosis are desalination of seawater and brackish groundwater.

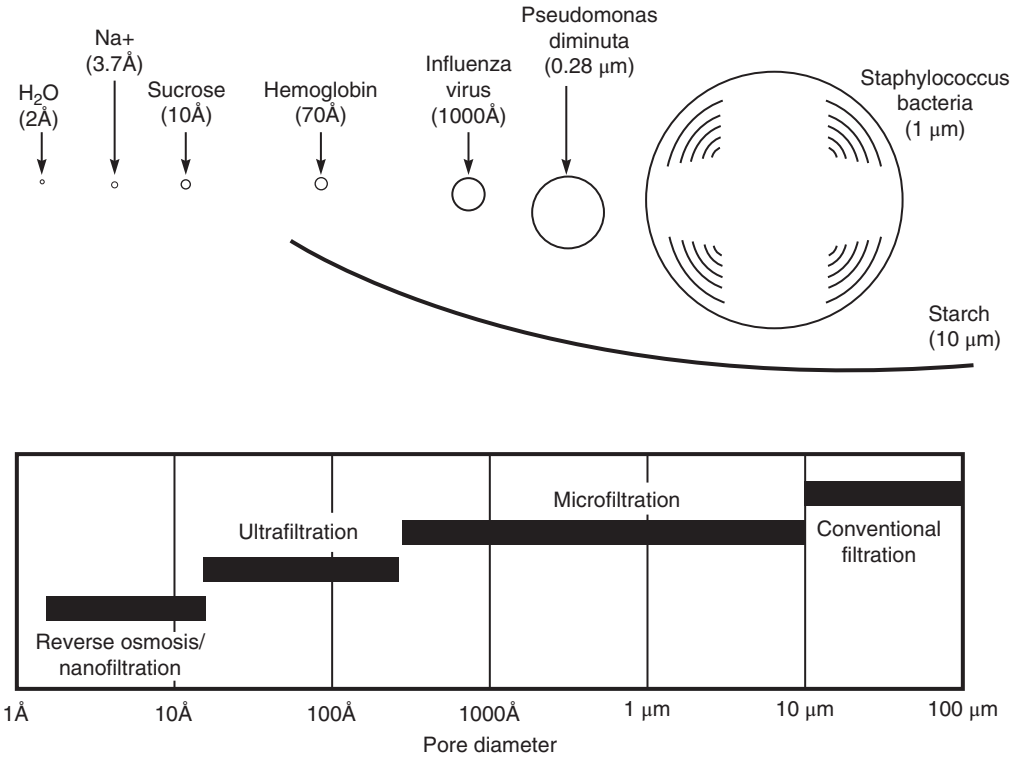

Figure 1.6 *Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. RO membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic.*

Reverse osmosis, ultrafiltration, and microfiltration are all directed to removing an undesired substance from water. From Figure 1.6, the typical pore diameter of a microfiltration membrane is about 1 μm. This is 100-fold larger than the average ultrafiltration pore and 1000-fold larger than the (nominal) diameter of pores in reverse osmosis membranes. Because flux is proportional to the square of the pore diameter, the permeance (that is, flux per unit transmembrane pressure difference ($J/\Delta p$)) of microfiltration membranes is enormously higher than that of ultrafiltration membranes, which in turn is much higher than that of reverse osmosis membranes. These differences significantly impact the operating pressure and the way that these membranes are used industrially. Reverse osmosis membranes typically operate at transmembrane pressures of 10–100 bar, ultrafiltration membranes at 0.2–5 bar, and microfiltration membranes at below 0.5 bar.

1.5.2 Electrodialysis

The fourth mature membrane process is electrodialysis (Chapter 11), 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 filter-press principle and containing several hundred individual cells, each bounded by an

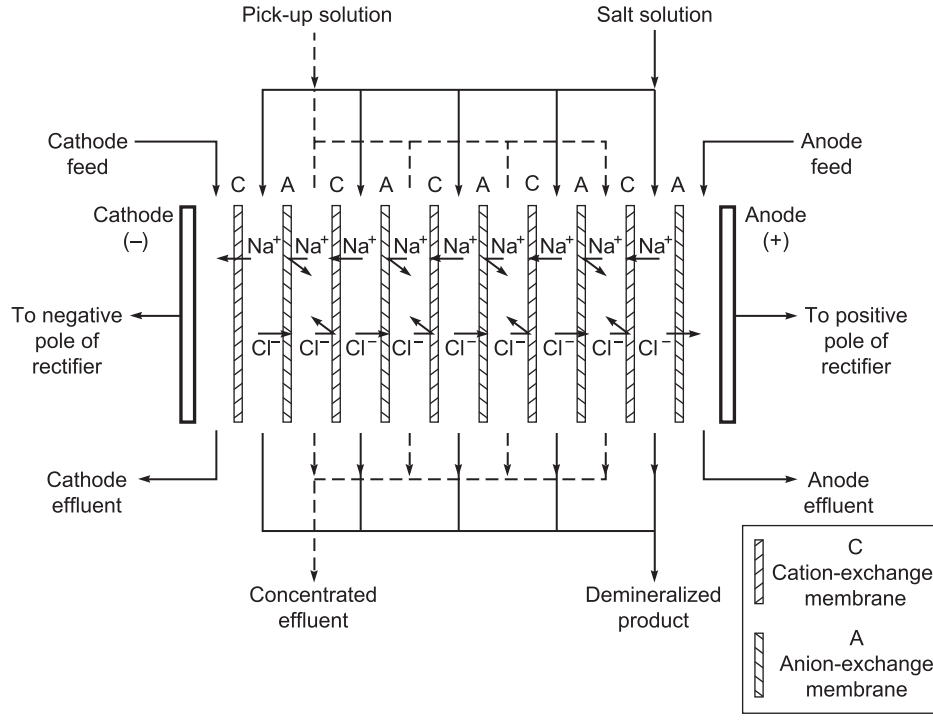

Figure 1.7 *Schematic diagram of an electrodialysis process.*

anion exchange membrane on one side and a cation exchange membrane on the other. Salt solution flows through every other cell; a much slower flow of pick-up solution flows through the adjacent cells. When a current is applied across the stack, anions and cations in the solutions carry the current toward their respective counter-charged electrodes. As a consequence, salt is removed from the salty feed solution cells, forming a demineralized product solution. The removed salt is concentrated into the pick-up cells and is removed as a concentrated brine. A schematic of the process is shown in Figure 1.7. The principal application of electrodialysis is desalting of brackish groundwater.

1.5.3 Gas Separation

The final established process, with annual sales in the US$1–2 billion/year range, is gas separation. At least 20 companies worldwide offer industrial systems for a variety of applications. In gas separation, a gas mixture at an elevated pressure is passed across the surface of a membrane that is selectively permeable to one component of the feed mixture; the membrane permeate is enriched in this species. The basic process is illustrated in Figure 1.8. Major current applications are the separation of hydrogen from nitrogen, argon and methane, used in refineries, petrochemical and ammonia plants; the production of nitrogen from air; the separation of carbon dioxide from methane in natural gas operations; the recovery of organic feedstocks in petrochemical plants; and the removal of C_{3+} hydrocarbons from raw natural gas. Membrane gas separation is an area of research interest, and the number of applications may increase.

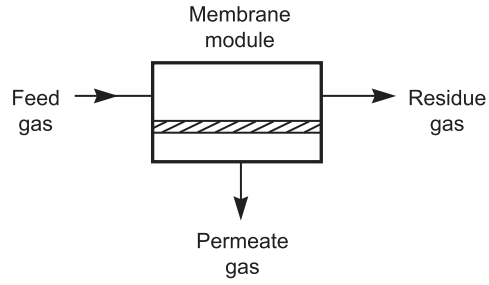

Figure 1.8 *Schematic diagram of the basic membrane gas separation process.*

In particular, much effort is being expended on the development of carbon dioxide/nitrogen processing schemes that could potentially handle the enormous streams of carbon-dioxide-laden flue gas that emanate from power plants, cement plants, steel mills, and the like.

1.5.4 Pervaporation

In pervaporation, a warm liquid mixture contacts one side of a membrane, and the permeate is removed as a vapor from the other. The driving force for the process is the low vapor pressure on the permeate side of the membrane, generated by cooling and condensing the permeate vapor. The attraction of pervaporation is that the separation obtained is proportional to the rate of permeation of the components of the liquid mixture through the selective membrane. Therefore, pervaporation offers the possibility of separating closely boiling mixtures and azeotropes, which are difficult to separate by distillation or other means.

A schematic of a pervaporation process in its simplest form, using a condenser to generate the permeate vacuum, is shown in Figure 1.9. Currently, the main industrial application of

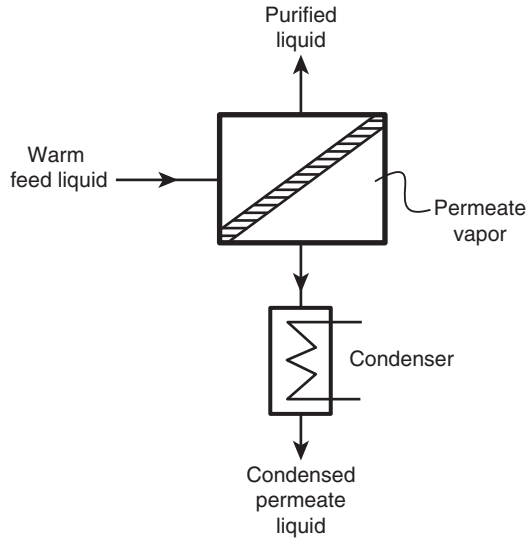

Figure 1.9 *Schematic diagram of the basic pervaporation process.*

pervaporation is the dehydration of organic solvents, in particular, the dehydration of ethanol solutions, a difficult separation problem because of the ethanol/water azeotrope at 95% ethanol. Pervaporation membranes that selectively permeate water can produce 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, for example of aromatics from aliphatics in refineries. Despite its apparent advantages, pervaporation has been in the 'developing' category for many years and has been slow to take off. Two related problems that have hampered its industrial success are scale-up and stability. A successful laboratory experiment requires only 100 cm^2 of membrane that can hold up under test conditions for a few days. An industrial process needs thousands of square meters of membrane stable enough to last a few years in a harsh organic environment. Organic polymer membranes do not fare well under this challenge. For this reason, many pervaporation membranes that have made it to industrial usage are ceramic based. Though stable when confronted with most organic components, these membranes are very expensive. In light of these issues, current annual worldwide sales of pervaporation units are probably no more than about US$50 million.

1.5.5 Hyperfiltration

Development of reverse osmosis to separate water from salt solutions using a pressure driving force has promoted the development of related polymeric membranes to separate organic solvent mixtures. The process is called hyperfiltration. The membranes used can be dense polymer films that separate permeants by the solution-diffusion process or they can be finely microporous membranes containing interconnected pores with diameters in the 5–25 Å range.

Today, hyperfiltration has only a few applications. One problem is the limited stability of polymeric membranes in organic solvent mixtures. A second problem is the high osmotic pressure that must be overcome to generate a solvent flow across the membrane. Nonetheless, a number of small, high value applications in the pharmaceutical and fine chemicals industries have developed [6]. Typical applications are the separation of catalysts or pharmaceutical products in the 200–300 MW range from solvents such as toluene or hexane.

1.5.6 Membrane Contactors

The most common use of membranes is as a filter in which a driving force of pressure across the membrane produces a flow of components from feed to permeate. There are also a number of applications where the function of the membrane is to provide a permeable barrier separating and preventing mixing of different fluids on either side of the membrane. The membrane may be selective for components in the fluids but this is not required. These devices, called membrane contactors, allow interchange of components between the fluids flowing on either side of the membrane. Permeation is usually produced by a difference in temperature or concentration. Membrane contactors are discussed in Chapter 13.

Membrane contactors are being used in a number of applications. One of the largest is in building air conditioners to allow water vapor to exchange between the dry ventilation air leaving the building and the humid hot fresh air entering. Another common application is to use a flow of nitrogen to remove dissolved oxygen from boiler feed water. A hollow fiber membrane contactor provides a large interchange area in a simple compact device. Applications of membrane contactors have grown in the last decades and this trend is likely to continue.

1.5.7 Carrier Transport

A number of processes are in the to-be-developed category in Table 1.1. Perhaps the most important of these is carrier transport (Chapter 12), which often employs liquid membranes containing a carrier agent. The carrier agent reacts with one component of a mixture on the feed side of the membrane and then diffuses across the membrane to release the component on the permeant side. The reformed carrier agent then diffuses back to the feed side. Thus, the carrier agent acts as a shuttle to selectively transport one component through the membrane.

Carrier transport can be used to separate gases, in which case transport is 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. Examples of carrier transport processes for gas and ion transport are shown in Figure 1.10.

Because carrier transport 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. This one fact has maintained interest in the technology for the past 40 years, but no commercial applications have developed. The principal problems are the physical instability of the liquid membrane and the chemical instability of the carrier agent, both of which have yet to be satisfactorily solved.

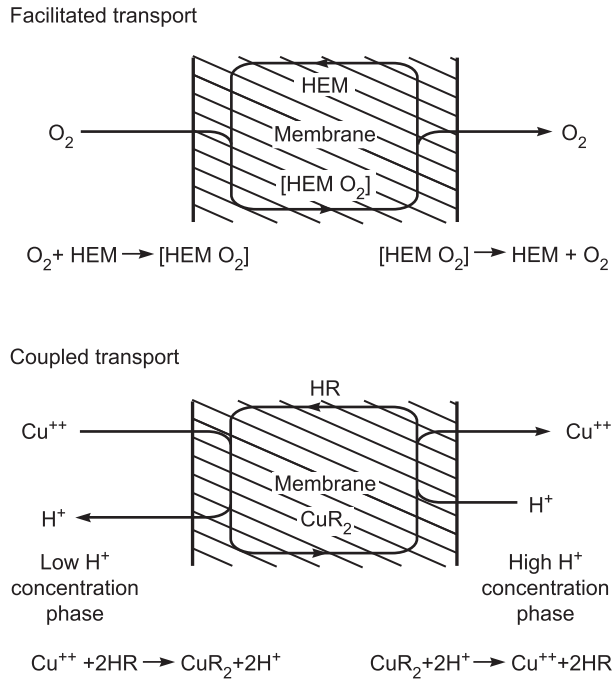

Figure 1.10 *Schematic examples of carrier-facilitated transport of gas and ions. The gas-transport example shows the transport of oxygen across a membrane using hemoglobin dissolved in water as the carrier agent. The ion-transport example shows the transport of copper ions across a membrane using a liquid ion-exchange reagent dissolved in a water immiscible solvent as the carrier agent.*

1.5.8 Medical Applications

The largest application of membranes in medicine is to remove toxic metabolites from blood in patients suffering from kidney failure. The first successful artificial kidney was based on cellophane (regenerated cellulose) dialysis membranes and was developed in 1943–1944. Many changes have been made since then. Currently, most artificial kidneys are based on hollow fiber membranes formed into modules having a membrane area of about 1 m^2; their use is illustrated in Figure 1.11. Blood is circulated through the center of the fiber; 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 slow, usually requiring several hours to remove the required amount of the metabolite from the patient, and must be repeated a couple of times per week. In terms of membrane area used and dollar value of the product, artificial kidneys are the single largest application of membranes.

Following the success of the artificial kidney, similar devices were developed to remove carbon dioxide from, and deliver oxygen to, the blood. These so-called artificial lungs are used in surgical procedures during which the patient's lungs cannot function. The dialysate fluid shown in Figure 1.11 is replaced with a carefully controlled sweep gas containing oxygen, which is delivered to the blood, and carbon dioxide, which is removed. These two medical applications of membranes are described in Chapter 14.

Another major medical use of membranes is in controlled drug delivery, also described in Chapter 14. Controlled drug delivery can be achieved by a wide range of techniques, many of which involve membranes; a simple example is the transdermal patch illustrated in Figure 1.12. In this device, designed to adhere to and deliver drugs through the skin, drug is contained in a reservoir that is separated from the skin by a membrane. With such a system, the release of drug through the membrane is constant as long as a constant concentration of drug is maintained within the device. A constant concentration is maintained if the reservoir contains a saturated solution and sufficient excess of solid drug. Systems that operate on this principle are used to moderate delivery of drugs such as nitroglycerine (for angina), nicotine (for smoking cessation), fentanyl (for pain), and estradiol (for hormone replacement therapy) through the skin. Other devices using osmosis or biodegradation as the rate-controlling mechanism are produced as implants and tablets.

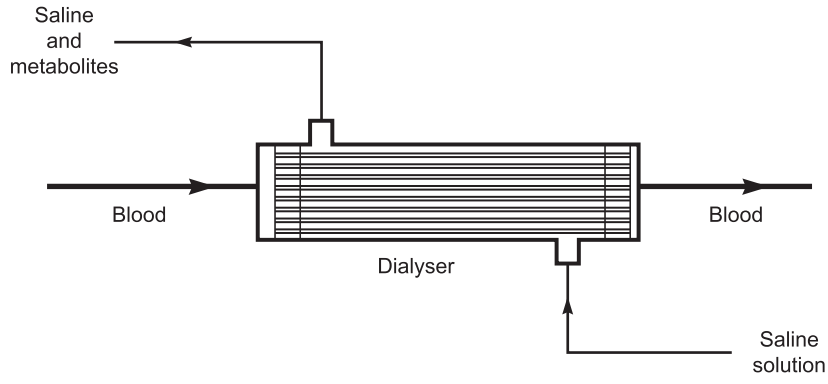

Figure 1.11 *Schematic of a hollow fiber artificial kidney dialyzer used to remove urea and other toxic metabolites from blood. About 100 million of these devices are used every year.*

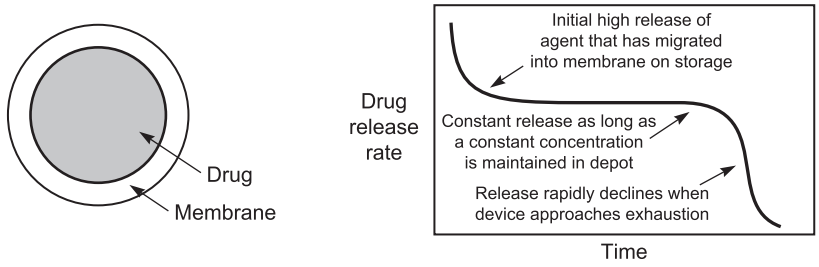

Diagram and release curve for a simple reservoir system

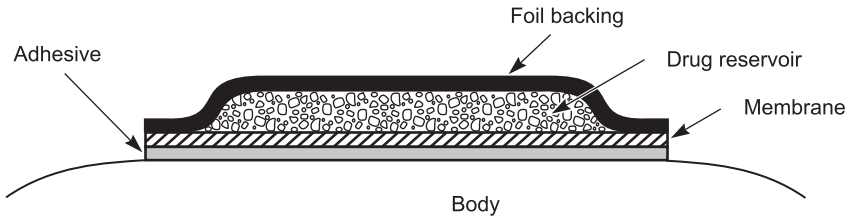

Figure 1.12 *Schematic of transdermal patch in which the rate of delivery of drug to the body is controlled by a polymer membrane. Such patches are used to deliver many drugs including nitroglycerine, estradiol, nicotine, and scopolamine.*

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