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Overview of Membrane Science and Technology

1.1 Introduction

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In controlled drug delivery, 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.

This book provides a general introduction to membrane science and technology. Chapters 2–4 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 facilitated transport is covered next, followed by a chapter reviewing the medical applications of membranes. The book closes with a chapter that describes various minor or yet-to-be-developed membrane processes, including membrane reactors, membrane contactors, and piezodialysis.

1.2 Historical Development of Membranes

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 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, particularly Elford [2], Zsigmondy and Bachmann [3], and Ferry [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 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 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 in only a few laboratory and small, specialized industrial applications. No significant membrane industry existed, and total annual sales of membranes for all industrial applications probably did not exceed US\$20 million in 2012 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. Solutions to each of these problems have been developed during the last 40 years, 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, anisotropic reverse osmosis membranes [5]. These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable 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 a potentially practical 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 and was a major factor in the development of ultrafiltration and microfiltration. The development of electrodialysis was also aided by OSW funding.

Concurrent with the development of these industrial applications of membranes was the independent development of membranes for medical separation processes, in particular, the artificial kidney. Kolf and Berk [6] had demonstrated the first successful artificial kidney in The Netherlands in 1945. 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. More than 800 000 people are now sustained by artificial kidneys and a further million people undergo open-heart surgery each year, a procedure made possible by development

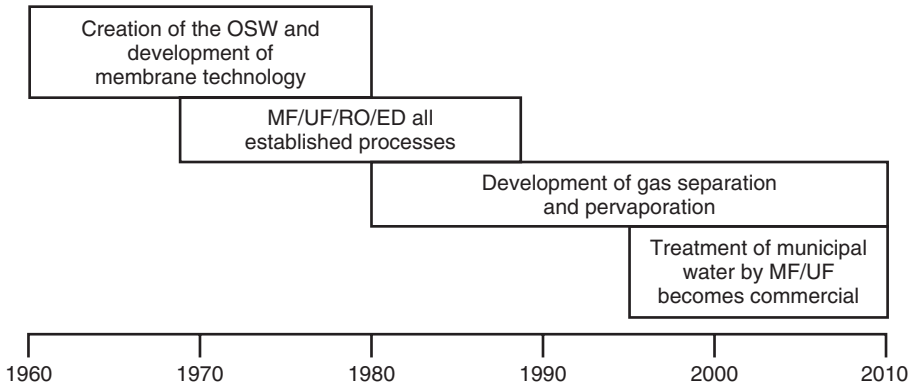


Figure 1.1 The development of the membrane separation industry, 1960–2010

of the membrane blood oxygenator. The sales of these devices comfortably exceed the total industrial membrane separation market. Another important medical application of membranes is for controlled drug delivery systems. A key figure in this area was Alex Zaffaroni, who founded Alza, a company dedicated to developing these products, in 1966. The membrane techniques developed by Alza and its competitors are widely used in the pharmaceutical industry to improve the efficiency and safety of drug delivery.

The modern membrane separation industry began in the 1960s. The creation of this 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 for making high-performance membranes. Using these processes, membranes with selective layers as thin as $0.1\mu\text{m}$ or less are now being produced by a number of 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.

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, ultrafiltration, reverse osmosis, and electrodialysis were all established processes. The third phase, which began in the 1980s, was the emergence of industrial membrane gas separation processes. The first major product was the Monsanto Prism[®] membrane for hydrogen separation, introduced in 1980 [7]. 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. Another development of the 1980s was the introduction by GFT, a small German engineering company, of the first commercial pervaporation systems for dehydration of alcohol and other solvents. Pervaporation has been slow to take off and 2010 sales were still not more than \$20 million. However, the development of bioethanol from biomass has produced a new, very large potential market for the technology, which may lead to future growth.

The final development phase, which began in the mid-1990s, was the development of reliable, economical microfiltration/ultrafiltration systems for the treatment of municipal water sources and for use in membrane bioreactors in sewage treatment plants. These applications were targets for membrane developers as early as the 1960s, but membrane fouling leading to low fluxes could not be overcome. In the late 1980s, Dr. Kazuo Yamamoto began to develop low-pressure, submerged air-sparged membranes [8]. It took another 10 years for companies like Kubota, Mitsubishi Rayon, and Zenon to scale up and bring these ideas to the commercial stage, and by the late 1990s, commercial systems 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 competitive with conventional biological treatment in terms of price and cost, and produce a far superior treated water product.

1.3 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. 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 or consisting of some form of layered structure. A normal filter meets this definition of a membrane, but, by convention, the term filter is usually limited to structures that separate particulate suspensions larger than 1–10 μm . The principal types of membrane are shown schematically in Figure 1.2 and are described briefly below.

1.3.1 Isotropic Membranes

1.3.1.1 Microporous Membranes

A microporous membrane is very similar in 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, on 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 will 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.

1.3.1.2 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

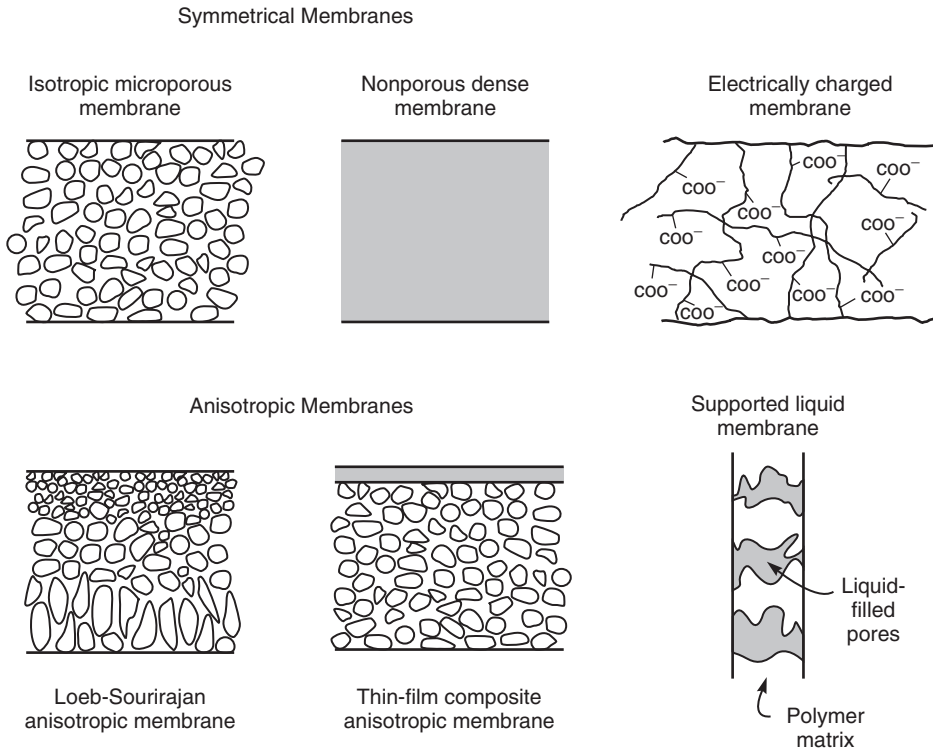


Figure 1.2 Schematic diagrams of the principal types of membranes

potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can separate permeants of similar size if the permeant concentrations in the membrane material (that is, their solubilities) differ significantly. Most gas separation, pervaporation, and reverse osmosis membranes use dense membranes to perform the separation. Usually these membranes have an anisotropic structure to improve the flux.

1.3.1.3 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 positively charged ions is referred to as an anion exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing fixed 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.

1.3.2 Anisotropic 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 thicknesses of about 20 μm . The development of novel membrane fabrication techniques to produce anisotropic membrane structures was one of the major breakthroughs of membrane technology during the past 40 years. Anisotropic membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. The surface layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers. 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 anisotropic membranes are so great that almost all commercial processes use such membranes.

1.3.3 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, in recent years, 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 liquid films are being developed for carrier facilitated transport processes.

1.4 Membrane Processes

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

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

The range of application of the three pressure-driven membrane water separation processes – reverse osmosis, ultrafiltration, and microfiltration – is illustrated in Figure 1.3. Ultrafiltration (Chapter 6) and microfiltration (Chapter 7) are basically similar in that the mode of separation is molecular sieving through increasingly fine pores. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μm

Table 1.1 Membrane technologies addressed in this book

Category	Process	Status
Developed industrial membrane separation technologies	Microfiltration Ultrafiltration Reverse osmosis Electrodialysis	Well established unit operations. No major breakthroughs seem imminent
Developing industrial membrane separation technologies	Gas separation Pervaporation	A number of plants have been installed. Market size and number of applications served are expanding
To-be-developed industrial membrane separation technologies	Carrier-facilitated transport Membrane contactors Piezodialysis, and so on	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

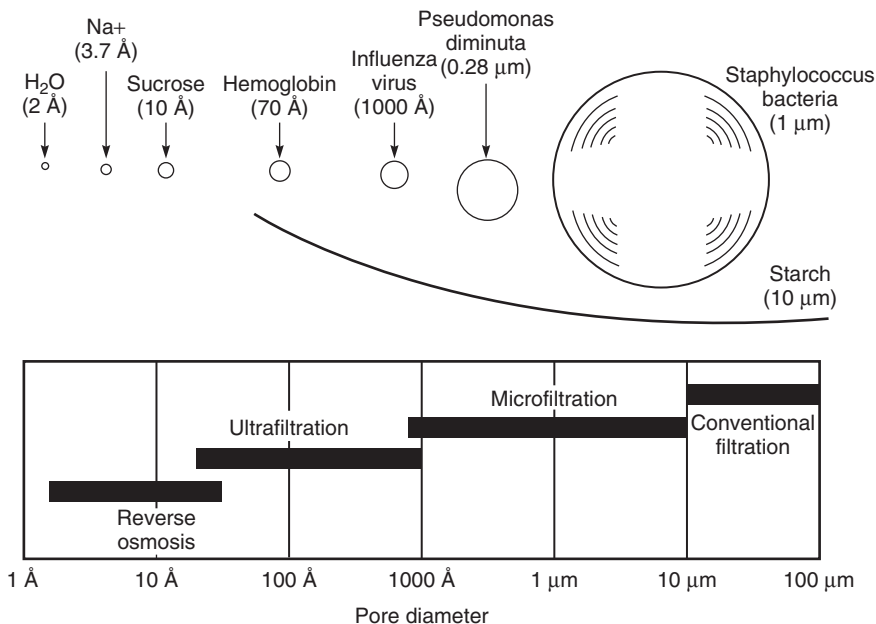


Figure 1.3 Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic

in diameter. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. The mechanism of separation by reverse osmosis membranes is quite different. In reverse osmosis membranes (Chapter 5), 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. The accepted mechanism of transport through these membranes is called 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 principal application of reverse osmosis is desalination of brackish groundwater or seawater.

Although reverse osmosis, ultrafiltration, and microfiltration are conceptually similar processes, the difference in pore diameter (or apparent pore diameter) produces dramatic differences in the way the membranes are used. A simple model of liquid flow through these membranes describes the membranes as a series of cylindrical capillary pores of diameter d . The liquid flow through a pore (q) is given by Poiseuille's Law as:

$$q = \frac{\pi d^4}{128 \mu \ell} \times \Delta p \quad (1.1)$$

where Δp is the pressure difference across the pore, μ is the liquid viscosity, and ℓ is the pore length. The flux, or flow per unit membrane area, is the sum of all the flows through the individual pores and so is given by:

$$J = N \times \frac{\pi d^4}{128 \mu \ell} \times \Delta p \quad (1.2)$$

where N is the number of pores per square centimeter of membrane.

For membranes of equal pore area and porosity (ε), the number of pores per square centimeter is proportional to the inverse square of the pore diameter. That is,

$$N = \varepsilon \times \frac{4}{\pi d^2} \quad (1.3)$$

It follows that the flux through membranes of equal porosity, given by combining Equations 1.2 and 1.3, is

$$J = \frac{\Delta p \varepsilon}{32 \mu \ell} \times d^2 \quad (1.4)$$

From Figure 1.3, the typical pore diameter of a microfiltration membrane is 10 000 Å. 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 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.

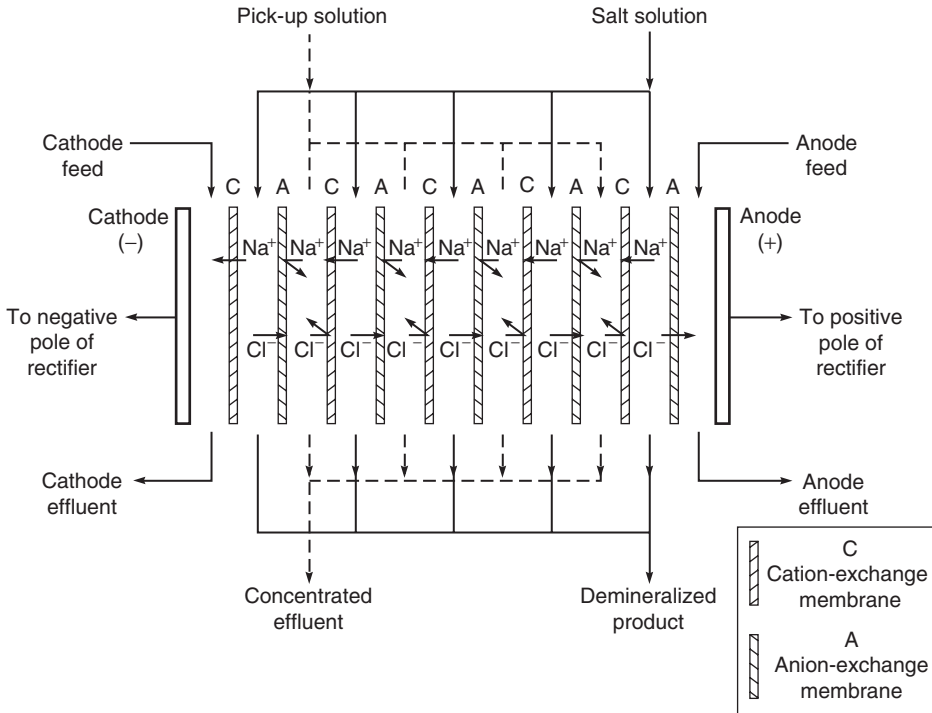


Figure 1.4 Schematic diagram of an electrodialysis process

The fourth fully developed membrane process is electrodialysis (Chapter 10), 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 formed by a pair of anion- and cation-exchange membranes. The principal application of electrodialysis is the desalting of brackish groundwater. 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. A schematic of the process is shown in Figure 1.4.

Table 1.1 shows two developing industrial membrane separation processes: gas separation with polymer membranes (Chapter 8) and pervaporation (Chapter 9). Gas separation with membranes is the more advanced of the two techniques; at least 20 companies worldwide offer industrial, membrane-based gas separation systems for a variety of applications. Only a handful of companies currently offer industrial pervaporation systems. 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 1.5. Major current applications of gas separation membranes are the separation of hydrogen from nitrogen, argon, and methane in ammonia plants; the production of

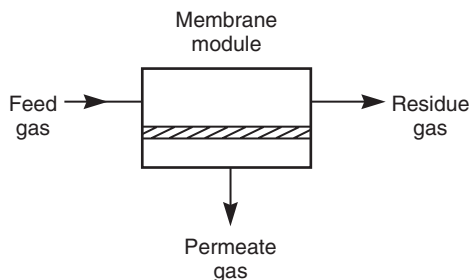


Figure 1.5 Schematic diagram of the basic membrane gas separation process

nitrogen from air; and the separation of carbon dioxide from methane in natural gas operations. Membrane gas separation is an area of considerable current research interest, and the number of applications is expanding rapidly.

Pervaporation is a relatively new process that has 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. 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 or azeotropes that are difficult to separate by distillation or other means. A schematic of a simple pervaporation process using a condenser to generate the permeate vacuum is shown in Figure 1.6. Currently,

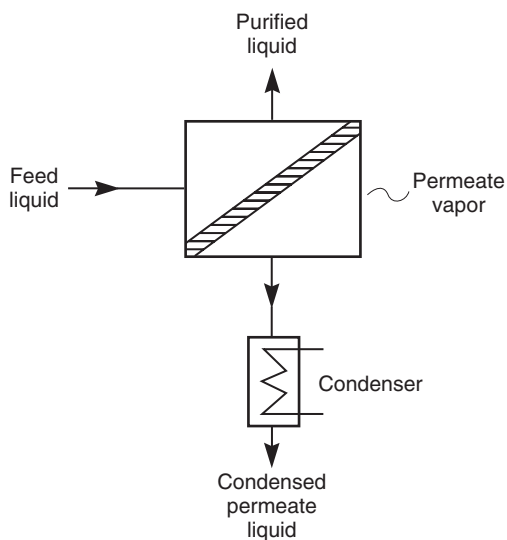
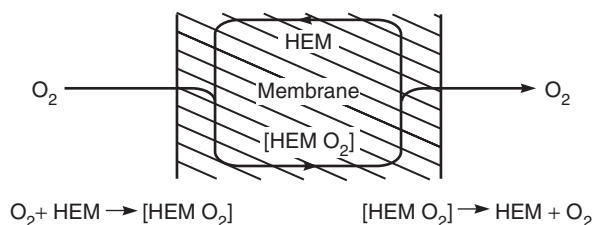


Figure 1.6 Schematic diagram of the basic pervaporation process

Facilitated transport



Coupled transport

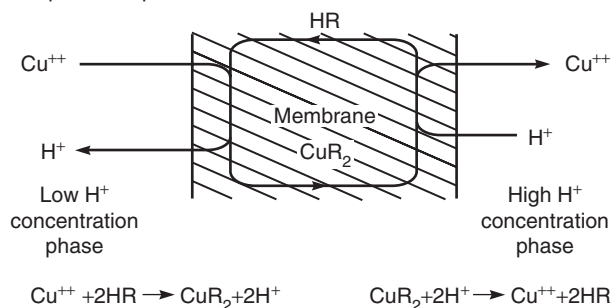


Figure 1.7 Schematic examples of carrier facilitated transport of gas and ions. The gas transport example shows the transport of oxygen across a membrane using hemoglobin dissolved in water as the carrier agent. The ion transport example shows the transport of copper ions across a membrane using a liquid ion exchange reagent dissolved in a water immiscible solvent as the carrier agent

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.

A number of other industrial membrane processes are placed in the category of to-be-developed technologies in Table 1.1. Perhaps the most important of these is carrier facilitated transport (Chapter 11), which often employs liquid membranes containing a complexing or 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 permeant on the product side of the membrane. The reformed carrier agent then diffuses back to the feed side of the membrane. Thus, the carrier agent 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

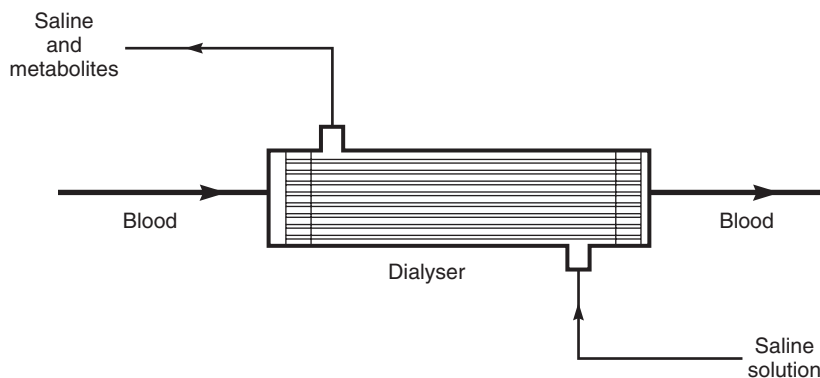


Figure 1.8 Schematic of a hollow fiber artificial kidney dialyser used to remove urea and other toxic metabolites from blood. About 100 million of these devices are used every year

hydroxyl ions in the other direction. This process is sometimes called coupled transport. Examples of carrier facilitated transport processes for gas and ion transport are shown in Figure 1.7.

Because the carrier facilitated transport process employs a reactive carrier species, very high membrane selectivities can be achieved. These selectivities are often far larger than the selectivities achieved by other membrane processes. This one fact has maintained interest in facilitated transport for the past 40 years, but no commercial applications have developed. The principal problem is the physical instability of the liquid membrane and the chemical instability of the carrier agent. In recent years, a number of potential solutions to this problem have been developed, which may yet make carrier facilitated transport a viable process.

The membrane separation processes described above represent the bulk of the industrial membrane separation industry. Another process, dialysis, is not used industrially but is used on a large scale in medicine 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 1945. Over the past 60 years, many changes have been made. Currently, most artificial kidneys are based on hollow-fiber membranes formed into modules having a membrane area of about 1 m^2 ; the process is illustrated in Figure 1.8. 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 or two times per week. In terms of membrane area used and dollar value of the membrane produced, artificial kidneys are the single largest application of membranes.

Following the success of the artificial kidney, similar devices were developed to remove carbon dioxide and deliver oxygen to the blood. These so-called artificial lungs are used in surgical procedures during which the patient's lungs cannot function.

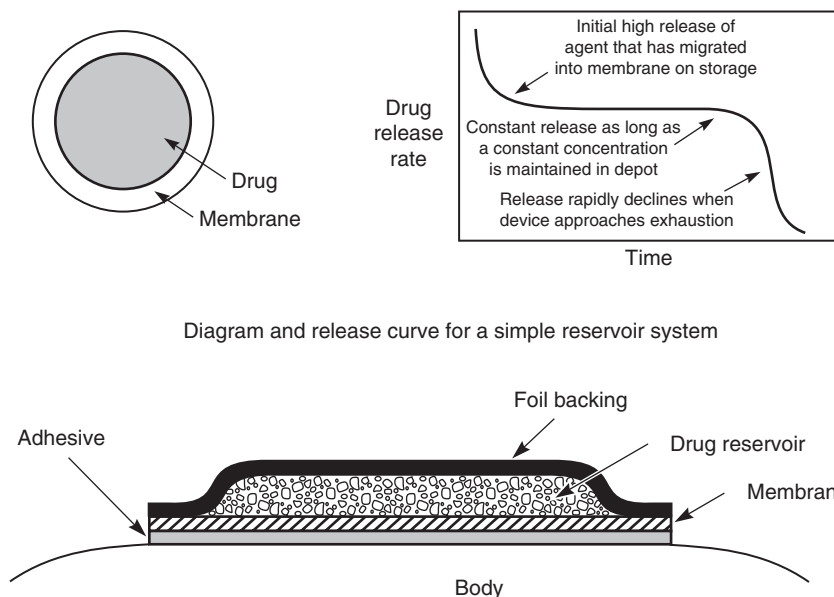


Diagram and release curve for a simple reservoir system

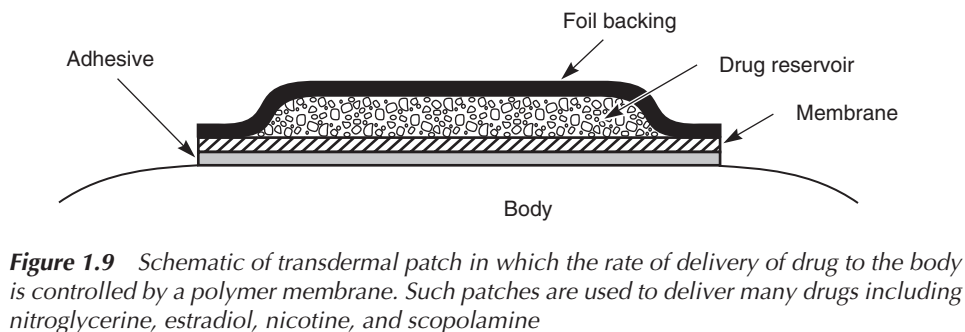


Figure 1.9 Schematic of transdermal patch in which the rate of delivery of drug to the body is controlled by a polymer membrane. Such patches are used to deliver many drugs including nitroglycerine, estradiol, nicotine, and scopolamine

The dialysate fluid shown in Figure 1.8 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 12.

Another major medical use of membranes is in controlled drug delivery (Chapter 12). Controlled drug delivery can be achieved by a wide range of techniques, most of which involve membranes; a simple example is illustrated in Figure 1.9. In this device, designed to deliver drugs through the skin, drug is contained in a reservoir surrounded by a membrane. With such a system, the release of drug 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 using this principle are used 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. The total market of controlled release pharmaceuticals is comfortably above US\$3 billion per year.

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