MEMBRANE TECHNOLOGY AND APPLICATIONS

SECOND EDITION

Richard W. Baker

Membrane Technology and Research, Inc.
Menlo Park, California

John Wiley & Sons, Ltd

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PREFACE

My introduction to membranes was as a graduate student in 1963. At that time membrane permeation was a sub-study of materials science. What is now called membrane technology did not exist, nor did any large industrial applications of membranes. Since then, sales of membranes and membrane equipment have increased more than 100-fold and several tens of millions of square meters of membrane are produced each year—a membrane industry has been created.

This membrane industry is very fragmented. Industrial applications are divided into six main sub-groups: reverse osmosis; ultrafiltration; microfiltration; gas separation; pervaporation and electrodialysis. Medical applications are divided into three more: artificial kidneys; blood oxygenators; and controlled release pharmaceuticals. Few companies are involved in more than one sub-group of the industry. Because of these divisions it is difficult to obtain an overview of membrane science and technology; this book is an attempt to give such an overview.

The book starts with a series of general chapters on membrane preparation, transport theory, and concentration polarization. Thereafter, each major membrane application is treated in a single 20-to-40-page chapter. In a book of this size it is impossible to describe every membrane process in detail, but the major processes are covered. However, medical applications have been short-changed somewhat and some applications—fuel cell and battery separators and membrane sensors, for example—are not covered at all.

Each application chapter starts with a short historical background to acknowledge the developers of the technology. I am conscious that my views of what was important in the past differ from those of many of my academic colleagues. In this book I have given more credit than is usual to the engineers who actually made the processes work.

Readers of the theoretical section (Chapter 2) and elsewhere in the book will see that membrane permeation is described using simple phenomenological equations, most commonly, Fick's law. There is no mention of irreversible thermodynamics. The irreversible thermodynamic approach to permeation was very fashionable when I began to work with membranes in the 1960s. This approach has the appearance of rigor but hides the physical reality of even simple processes behind a fog of tough equations. As a student and young researcher, I struggled with irreversible thermodynamics for more than 15 years before finally giving up in the 1970s. I have lived happily ever after.

Finally, a few words on units. Because a great deal of modern membrane technology originated in the United States, the US engineering units—gallons, cubic feet, and pounds per square inch—are widely used in the membrane industry. Unlike the creators of the Pascal, I am not a worshipper of mindless uniformity. Metric units are used when appropriate, but US engineering units are used when they are the industry standard.

ACKNOWLEDGMENTS FOR THE FIRST EDITION

As a school boy I once received a mark of $\frac{1}{2}$ out of a possible 20 in an end-of-term spelling test. My spelling is still weak, and the only punctuation I ever really mastered was the period. This made the preparation of a polished final draft from my yellow notepads a major undertaking. This effort was headed by Tessa Ennals and Cindi Wieselman. Cindi typed and retyped the manuscript with amazing speed, through its numerous revisions, without complaint. Tessa corrected my English, clarified my language, unsplit my infinitives and added every semicolon found in this book. She also chased down a source for all of the illustrations used and worked with David Lehmann, our graphics artist, to prepare the figures. It is a pleasure to acknowledge my debt to these people. This book would have been far weaker without the many hours they spent working on it. I also received help from other friends and colleagues at MTR. Hans Wijmans read, corrected and made numerous suggestions on the theoretical section of the book (Chapter 2). Ingo Pinnau also provided data, references and many valuable suggestions in the area of membrane preparation and membrane material sciences. I am also grateful to Kenji Matsumoto, who read the section on Reverse Osmosis and made corrections, and to Heiner Strathmann, who did the same for Electrodialysis. The assistance of Marcia Patten, who proofed the manuscript, and Vivian Tran, who checked many of the references, is also appreciated.

ACKNOWLEDGMENTS FOR THE SECOND EDITION

Eighteen months after the first edition of this book appeared, it was out of print. Fortunately, John Wiley & Sons, Ltd agreed to publish a second edition, and I have taken the opportunity to update and revise a number of sections. Tessa Ennals, long-time editor at Membrane Technology and Research, postponed her retirement to help me finish the new edition. Tessa has the standards of an earlier time, and here, as in the past, she gave the task nothing but her best effort. I am indebted to her, and wish her a long and happy retirement. Marcia Patten, Eric Peterson, David Lehmann, Cindy Dunnegan and Janet Farrant assisted Tessa by typing new sections, revising and adding figures, and checking references, as well as helping with proofing the manuscript. I am grateful to all of these colleagues for their help.

1 OVERVIEW OF MEMBRANE SCIENCE AND TECHNOLOGY

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 to 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, which 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.

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

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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 2003 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 30 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.

Concurrently with the development of these industrial applications of membranes was the independent development of membranes for medical separation

processes, in particular, the artificial kidney. W.J. Kolf [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 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 period from 1960 to 1980 produced a significant change in the status of membrane technology. 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 μm 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. By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide.

The principal development in the 1980s was the emergence of industrial membrane gas separation processes. The first major development 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 evolving and expanding rapidly; further substantial growth will be seen in the coming years. 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. More than 100 ethanol and isopropanol pervaporation dehydration plants have now been installed. Other pervaporation applications are at the early commercial stage.

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

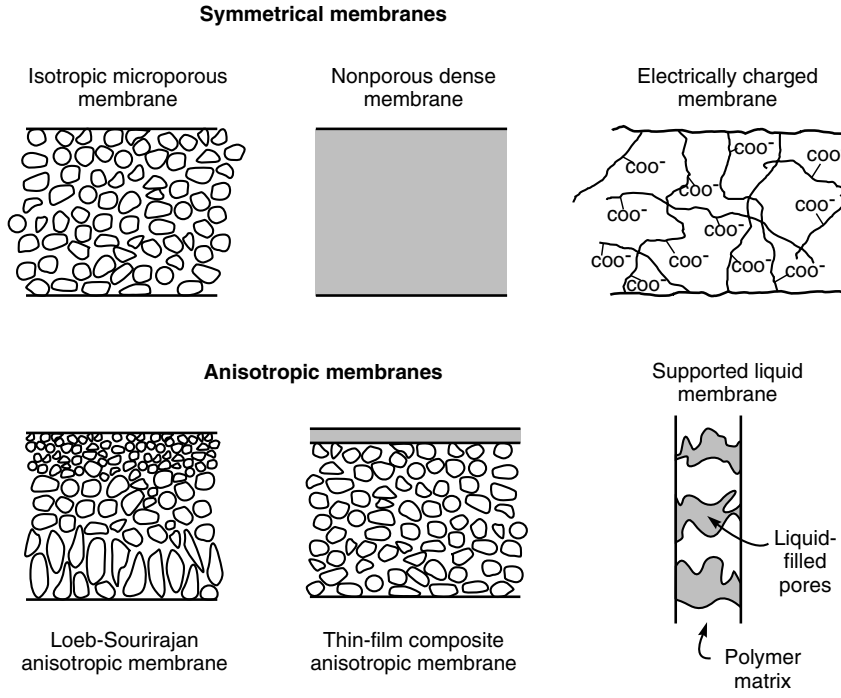

Figure 1.1 Schematic diagrams of the principal types of membranes

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 to 10 μm. The principal types of membrane are shown schematically in Figure 1.1 and are described briefly below.

Isotropic Membranes

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 to 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.

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 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 their concentration in the membrane material (that is, their solubility) differs 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.

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.

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 about 20 μm thickness. The development of

novel membrane fabrication techniques to produce anisotropic membrane structures was one of the major breakthroughs of membrane technology during the past 30 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.

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.

Membrane Processes

Six developed and a number of developing and yet-to-be-developed industrial membrane 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 four 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 1.2. 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 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

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, etc.	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

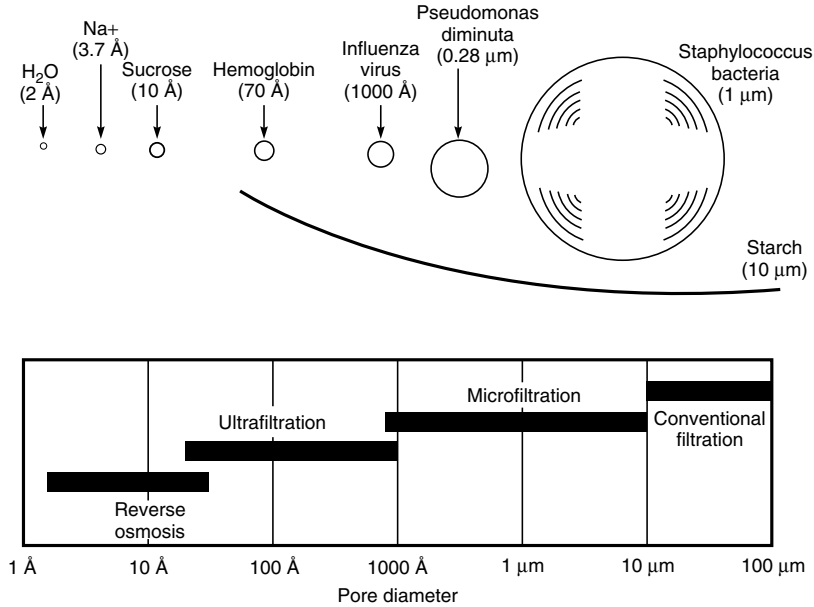

Figure 1.2 Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic

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 is to describe 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:

$$q = \frac{\pi d^4}{128\ \mu\ell} \cdot \Delta p \tag{1.1}$$

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:

$$J = N \cdot \frac{\pi d^4}{128\ \mu\ell} \cdot \Delta p \tag{1.2}$$

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,

$$N = \varepsilon \cdot \frac{4}{\pi d^2} \tag{1.3}$$

It follows that the flux, given by combining Equations (1.2) and (1.3), is

$$J = \frac{\Delta p \varepsilon}{32\ \mu\ell} \cdot d^2 \tag{1.4}$$

From Figure 1.2, 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 fluxes are proportional to the square of these pore diameters, 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.

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 1.3.

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 1.4. Major current applications

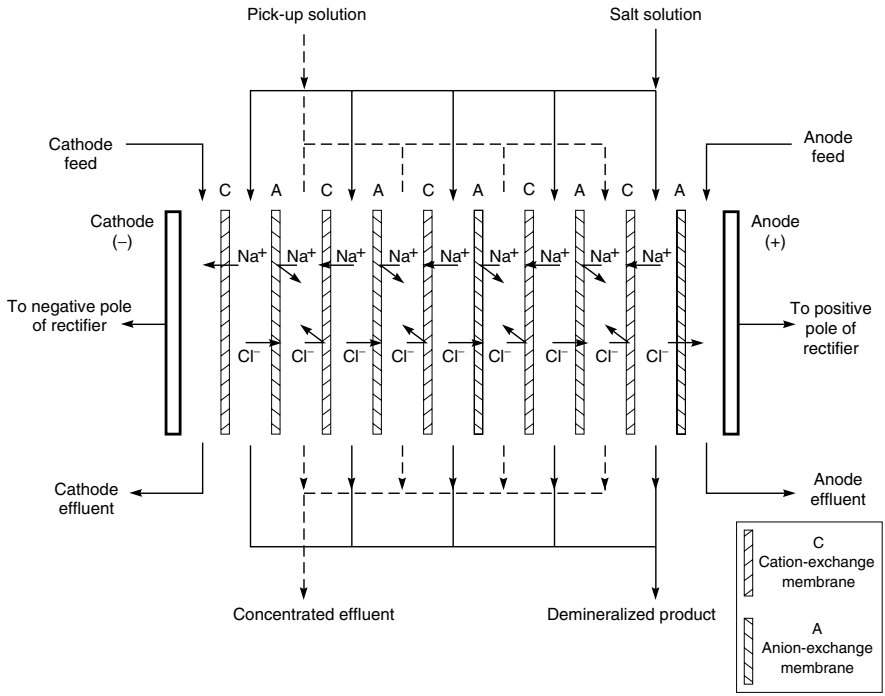

Figure 1.3 Schematic diagram of an electrodialysis process

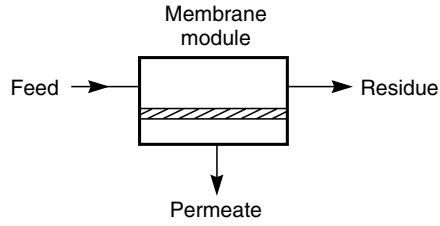

Figure 1.4 Schematic diagram of the basic membrane gas separation process

of gas separation membranes are the separation of hydrogen from nitrogen, argon and methane in ammonia plants; the production of 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 1.5. 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.

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.

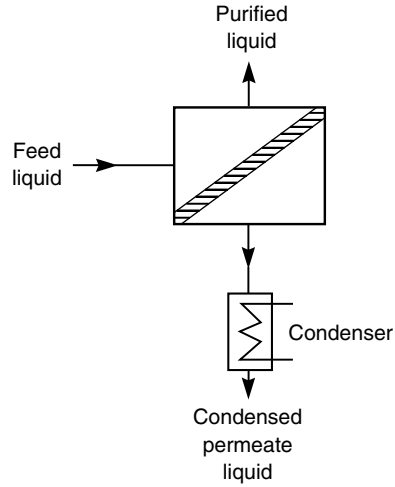

Figure 1.5 Schematic diagram of the basic pervaporation process

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. Examples of carrier facilitated transport processes for gas and ion transport are shown in Figure 1.6.

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 30 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 50 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 1.7. Blood is circulated through the center of the fiber, while isotonic

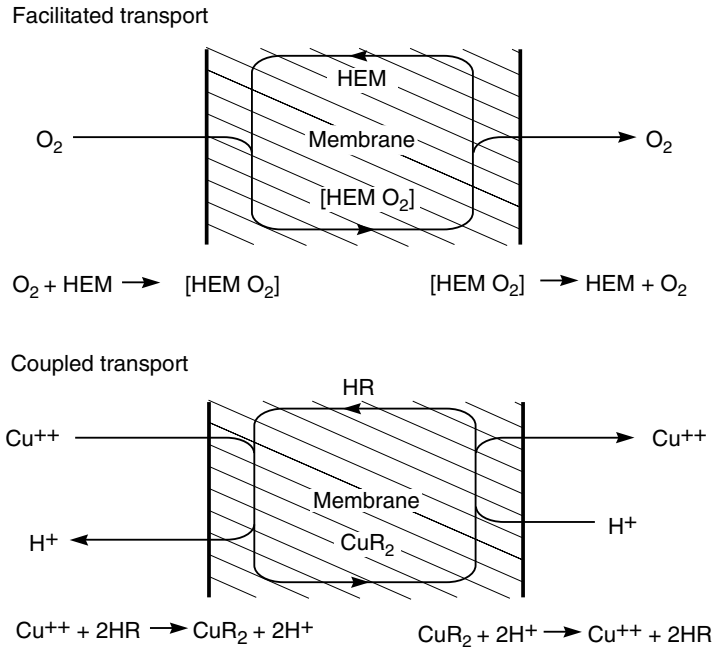

Figure 1.6 Schematic examples of carrier facilitated transport of gas and ions. The gas transport example shows the transport of oxygen across a membrane using hemoglobin as the carrier agent. The ion transport example shows the transport of copper ions across a membrane using a liquid ion-exchange reagent as the carrier agent

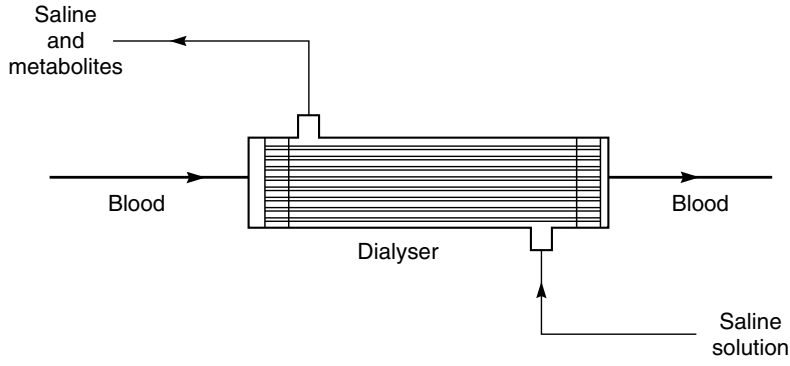

Figure 1.7 Schematic of a hollow fiber artificial kidney dialyser used to remove urea and other toxic metabolites from blood. About 100 million of these devices are used every year

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. The dialysate fluid shown in Figure 1.7 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 1.8. In this device, designed to deliver drugs through the skin, drug is contained in a reservoir surrounded by a membrane. With such a system,

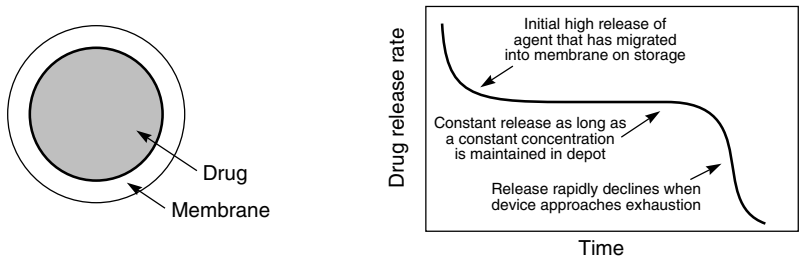

Diagram and release curve for a simple reservoir system

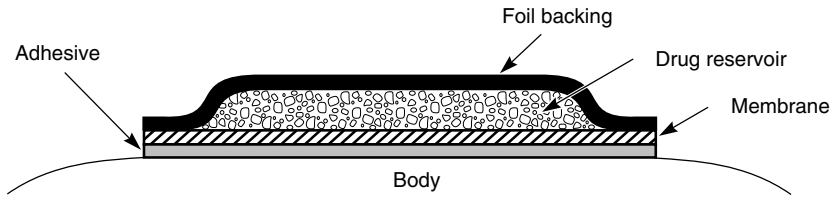

Figure 1.8 Schematic of transdermal patch in which the rate of delivery of drug to the body is controlled by a polymer membrane. Such patches are used to deliver many drugs including nitroglycerine, estradiol, nicotine and scopalamine

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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