1
Introduction

1.1
Overview of Membrane Science and Technology

The development of synthetic membranes and their practical application started a little over 100 years ago. Biological membranes, however, are as old as life on earth. As a vital part of the living cells, biological membranes fulfill a large number of sometimes complex mass and energy transport functions very efficiently and with minimal energy expenditure. They can transport individual chemical components selectively and under certain conditions, which may be controlled by specific components such as ligands or an electrical potential gradient. Biological membranes are extremely thin, in the range of several nanometers and most important, they are capable of so-called *active* transport, that is, transport without any external driving force, while synthetic membranes are much thicker, that is, in the range of several micrometers and the transport is the result of an external driving force. These facts explain the high efficiency of biological membranes.

Although synthetic membranes are extremely simple in their structures and functions compared with biological membranes, they have become key components in many technically and commercially relevant industrial processes. Today, synthetic membranes are used on a large scale to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, or to concentrate and fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors. They are also key components in energy conversion and storage systems such as batteries and fuel cells. In artificial organs, drug delivery systems or sensors and diagnostic devices membranes play a vital role in biomedical applications. They are also used to control the release rate of certain active agents such as fertilizers or pesticides from a reservoir.

Membranes and membrane processes were first introduced as an analytical tool in chemical and biomedical laboratories, but they developed very rapidly into industrial products and processes with significant technical and commercial impact.

The membranes used in various applications differ widely in their structure, their function, and the way they are operated in a given process. However, all membranes and membrane processes share several features that make them

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particularly attractive tools for the separation of molecular mixtures. The separation is performed by physical means at ambient temperature without chemically altering the constituents. This is important for applications in artificial organs and in many drug delivery systems, as well as in the food and drug industries or in downstream processing of bioproducts where temperature-sensitive substances must often be handled. Furthermore, membrane properties can be tailored and adjusted to specific separation tasks and membrane processes are often technically simpler and more energy efficient than conventional separation techniques and are equally as well-suited to large-scale continuous operations as to batch-wise treatment of very small quantities.

The applications of membranes and membrane processes can be divided into four characteristic areas as indicated in Table 1.1.

In addition to the state-of-the-art membrane processes indicated in Table 1.1 a number of new applications have recently been identified such as membrane contactors, membrane emulsifiers, or catalytic membrane reactors. Process intensification in the chemical industry and artificial organs in medical applications are based on membranes and will most likely increase their technical and commercial relevance.

Although synthetic membranes are widely used as valuable scientific and technical tools in a modern industrialized society, they are not very well defined and understood in terms of their structure and function. The most prominent association that many people have when thinking of a membrane resembles that of a filter, that is, a device capable of separating various components from a mixture according to their size.

However, a membrane can be much more complex in both structure and function. A membrane may be solid or liquid, homogeneous or heterogeneous, isotropic or anisotropic in its structure. A membrane can be a fraction of a micrometer or several millimeters thick. Its electrical resistance can vary from millions of ohms to a fraction of an ohm.

Another characteristic property of a membrane is its permselectivity, which is determined by differences in the transport rates of various components in the

Table 1.1 State-of-the-art membranes and their application.

Separation of molecular mixtures	Controlled release of active agents	Chemical and biochemical synthesis	Energy storage and conversion
Microfiltration, ultrafiltration, and reverse osmosis	Slow release of fertilizers and pesticides	Catalytic membrane reactors	Fuel cells and battery separators
Dialysis and electrodialysis	Drug delivery devices	Electrochemical synthesis	Reverse electrodialysis
Gas and vapor separation	Protective coatings	Bio-hybrid organs	Pressure retarded osmosis

membrane matrix. The permeability of a membrane is a measure of the rate at which a given component is transported through the membrane under specific conditions of concentration, temperature, pressure, and/or electrical potential. The transport rate of a component through a membrane is determined by membrane properties such as its structure and the chemical nature or electrical charges of the membrane material, by properties of the permeating component such as its size, its chemical nature, or electrical charge, and by an external driving force or forces such as concentration, pressure, or electrical potential gradients across the membrane. The transport of certain components through a membrane may be facilitated by so-called carrier components. These phenomena are referred to as *facilitated* or *coupled transport*.

The versatility of membrane structures and functions makes a precise and complete definition of a membrane rather difficult. In the most general sense a membrane is a barrier that separates and/or contacts two different regions and controls the exchange of matter and energy between the regions. The membrane can be a selective or a contacting barrier. In the first case, it controls the exchange of mass energy and electrical charges between the two regions separated by the membrane in a very specific manner; in the second case, its function is mainly to contact the two regions between which the transport occurs.

In contrast to biological membranes, which are capable of active transport, synthetic membranes are not nearly as complex in their structure or function. They have only passive transport properties and are less selective and energy efficient. In general, however, synthetic membranes have significantly higher chemical and mechanical stability, especially at elevated temperatures, than biological membranes. The selectivity of synthetic membranes is determined by their structure and the material they are made of. In porous membranes various components of a mixture are separated according to their size and the size of the membrane pores. In homogeneous or dense membranes components are separated according to their solubility and diffusivity in the membrane matrix or their electrical charges.

Structures, materials, and the mode of transport of typical synthetic membranes which are used today on a large scale are summarized in Table 1.2.

Table 1.2 Structures, materials, and separation mechanism of commercial synthetic membranes.

Membrane structures	Membrane materials	Transport mode and separation mechanism
Porous films	Polymers, ceramics, metals	Convection and diffusion through pores
Non-porous films	Polymers, metals, ceramics	Solution and diffusion in a solid film
Supported liquid films	Liquids in porous membranes	Solution and diffusion in a liquid film
Electrically charged barriers	Polymers, ceramics	Diffusion and migration through a film with fixed charges

The permeability of the membrane for different components, however, is only one parameter determining the flux through the membrane. Just as important as the permeability is the driving force acting on the permeating components. The generalized driving force for transport in membranes is the gradient in the electrochemical potential of the individual components. Some driving forces such as concentration, pressure, or temperature gradients can be applied to all components in contrast to an electrical potential driving force, which is only effective with charged components. The use of different membrane structures and driving forces has resulted in a number of rather different membrane processes such as reverse osmosis, micro-, ultra-, and nanofiltration, dialysis, electrodialysis, Donnan dialysis, pervaporation, gas separation, membrane contactors, membrane distillation, membrane-based solvent extraction, membrane reactors, and so on.

Even more heterogeneous than membrane structures and membrane processes are their practical applications. The large-scale industrial use of membranes began about 1970 with water desalination and purification to produce potable and high quality industrial water. Since then membranes have become a widely used tool in process engineering with significant technical and commercial impact. Today membrane processes are used in three main areas. The first area includes applications such as sea water desalination or waste water purification. Here, the use of membranes is technically feasible, but there are other processes such as distillation and biological treatment with which membranes must compete on the basis of overall economy. The second area includes applications such as the production of ultrapure water or the separation of molecular mixtures in the food and drug industry. Here, alternative techniques are available, but membranes offer a clear technical and commercial advantage. The third area includes membrane applications in artificial organs and therapeutic systems, where there are no reasonable alternatives to membrane operations.

With the development of new membranes having better separation efficiency and new membrane processes such as membrane contactors and membrane reactors becoming common unit operations in process engineering, the large-scale use of membranes is rapidly extending far beyond its present level.

1.2
History of Membrane Science and Technology

Synthetic membranes are a rather recent development and the technical use of membrane processes on a large scale began just 40 years ago. One of the first recorded studies of membrane phenomena and the discovery of osmosis dates back to the middle of the eighteenth century when Nollet [1] discovered that a pig's bladder preferentially permitted the passage of water when it was brought into contact on one side with a water–ethanol mixture and on the other side with pure water. Nollet was probably the first to recognize the relation between a semipermeable membrane and the osmotic pressure. More systematic studies on mass transport in semipermeable membranes were carried out by Graham [2] who studied the diffusion of gases through different media and discovered that rubber exhibits different permeabilities to different gases.

Most of the early studies on membrane permeation were carried out with natural materials such as animal bladders or gum elastics. The first artificially prepared semipermeable membranes were prepared by precipitating cupric ferrocyanide in a thin layer of porous porcelain and used by Pfeffer [3] in his fundamental studies on osmosis. The theoretical treatment and much of the interpretation of osmotic phenomena and mass transport through membranes is based on the studies of Fick [4] who interpreted diffusion in liquids as a function of concentration gradients, who interpreted diffusion in liquids as a function of concentration gradients, and van t'Hoff [5] who gave a thermodynamic explanation for the osmotic pressure of dilute solutions. With the classical publications of Donnan [6] describing the theory of membrane equilibria and membrane potentials in the presence of electrolytes, the early history of membrane science ends with most of the basic phenomena satisfactorily described and theoretically interpreted.

At the beginning of the twentieth century membrane science and technology entered a new phase. Bechhold [7] developed a method of making the first synthetic membranes by impregnating a filter paper with a solution of nitrocellulose in glacial acetic acid. These membranes could be prepared and accurately reproduced with different permeabilities by varying the ratio of acetic acid to nitrocellulose. Nitrocellulose membranes were also the first commercial membranes that became available in 1937 in a series with various pore sizes. These membranes were used in microbiological laboratories in analytical applications. The development of the first successfully functioning hemodialyzer by Kolff and Berk [8] in 1944 was the key to the large-scale application of membranes in the biomedical area.

In the early days of membrane science and technology membranes had mainly been a subject of scientific interest with only a few practical applications. This changed drastically from 1950 on, when the practical use of membranes in technically relevant applications became the main focus of interest and a significant membrane-based industry developed rapidly. Progress in polymer chemistry provided a large number of synthetic polymers which ultimately became available for the preparation of new membranes with specific transport properties plus good mechanical and thermal stability. Membrane transport properties were described by a comprehensive theory based on the thermodynamics of irreversible processes.

A second route for describing membrane processes was based on postulating certain membrane transport models, such as the pore flow and the solution-diffusion membrane model. The properties of ion-exchange membranes and their practical use were also the subjects of extensive studies.

A milestone in membrane science and technology was the development, by Loeb and Sourirajan [9] in 1962, of a reverse osmosis membrane based on cellulose acetate, which provided high salt rejection and high fluxes at moderate hydrostatic pressures. This was a major advance toward the application of reverse osmosis membranes as an effective tool for the production of potable water from the sea. The membrane developed by Loeb and Sourirajan had an asymmetric structure with a dense skin at the surface which determined the membrane selectivity and flux. This skin was supported by a highly porous substructure which provided the mechanical strength of the membrane. It was shown that the preparation of asymmetric cellulose acetate membranes was based on a phase inversion process in which a homogeneous polymer solution is converted into a two-phase system, that is, a solid polymer-rich phase providing the solid polymer structure and a polymer-lean phase forming the liquid-filled membrane pores. Soon, other synthetic polymers such as polyamides, polyacrylonitrile, polysulfone, polyethylene, and so on, were used as basic materials for the preparation of synthetic membranes. These polymers often showed better chemical and thermal stability than the cellulose esters. However, cellulose acetate remained the dominant material for the preparation of reverse osmosis membranes until the development of the composite membranes prepared by interfacial polymerization. These membranes showed significantly higher fluxes, higher rejection, and better chemical and mechanical stability than the cellulose acetate membranes.

The first membranes used in reverse osmosis desalination and other applications were manufactured as flat sheets and then installed in a so-called spiral-wound module. A different approach to membrane geometry was the development of self-supporting hollow fiber membranes which had an external diameter of about 100 μm and a wall thickness of only 6–10 μm. Asymmetric hollow fiber membranes are applied mainly in sea water desalination and in gas separation. Later capillary and tubular type membranes were developed. Capillary membranes which have an external diameter of 300–1000 μm are mainly used in hemodialysis. Tubular membranes with an external diameter of 1–2 cm are mainly used in ultrafiltration of solutions having a high content of solid materials.

Soon after the development of efficient membranes, appropriate membrane housing devices, called *modules*, were established. The criteria for the design of such modules included high membrane packing density, operation reliability, ease of membrane or module replacement, control of concentration polarization, and low costs. Today, membranes are mainly produced in three different configurations, that is, as flat sheets, as hollow fibers or capillaries, and as tubular devices. Flat sheet membranes are installed in so-called plate-and-frame or spiral-wound modules and are used in various applications such as reverse osmosis desalination and ultrafiltration of solutions or gas separation and pervaporation. Hollow fiber membrane modules consist of bundles of fibers in an appropriate housing and are mainly used in gas separation. Capillary membrane modules are constructed similarly to hollow fiber modules and are mainly used in medical applications, such as artificial kidneys and blood oxygenators.

Even earlier than the large-scale use of reverse osmosis for sea and brackish water desalination was the industrial scale application of electrodialysis. The history of electrodialysis goes back to the development of the first multi-cell stack. However, modern electrodialysis became a practical reality with the development of the first reliable ion-exchange membranes to have both good electrolyte conductivity and ion-permselectivity. Electrodialysis was first commercially used for the desalination of brackish water. The commercial success of electrodialysis was due to compact stacking of the membranes and the mode of operation referred to as *electrodialysis* *reversal*, which provided a periodic self-cleaning mechanism for the membrane stack and thus allowed long-term continuous operation at high concentrations of scaling materials without mechanical cleaning of the stack.

In the early 1980s a completely new area for the application of electrodialysis was opened up with the introduction of bipolar membranes for the recovery of acids and bases from the corresponding salt.

The large-scale separation of gases and vapors with membranes began in the 1970s. Originally, the aim of gas separation was to recover hydrogen from off-gases and to produce oxygen- or nitrogen-enriched air. Today however, a large number of other applications, such as the removal of CO_2 from natural gas or the recovery of organic vapors from off-gases, are typical applications for gas and vapor separation.

Pervaporation, which is closely related to vapor separation, has been studied extensively for more than four decades, and a large number of interesting potential applications have been pointed out, but so far very few large commercial plants have been built. Other applications of membranes which have been developed in recent years include the controlled release of drugs in therapeutic devices and the storage and conversion of energy in fuel cells and batteries. However, the commercially most important application of membranes today is in reverse osmosis water desalination and in hemodialysis and hemofiltration.

1.3
Advantages and Limitations of Membrane Processes

Membrane processes are considered in many cases to be very energy efficient compared with many other separation processes. They can easily be up- or down-scaled and are generally operated at ambient temperature avoiding any change or degradation of products. Their environmental impact is low since no hazardous chemicals are used or generated in membrane processes, that have to be discharged. Furthermore, the quality of products generated in membrane processes is generally quite high, thus, very few post-treatment procedures are required. In many applications such as water desalination and purification the membrane processes compete directly with the more conventional water treatment techniques. In desalination of sea and brackish water, for example, reverse osmosis and electrodialysis compete with distillation processes. Depending on local conditions, including water quality, energy cost, and the required capacity of the desalination plant, either electrodialysis, reverse osmosis, or distillation can be the most cost-efficient process. In water desalination the energy consumption in membrane processes is indeed significantly lower than in distillation. However, the required energy is only one cost factor. Investment and maintenance related costs often contribute significantly to the overall process costs. Other costs that must be considered are those for pre- and post-treatment procedures, the required product quality and the composition of the feed water. Furthermore, it must be taken into account that for instance, in reverse osmosis the pressure-generating pumps are driven either by electric or combustion engines. These engines usually have an efficiency of less than 40% in relation to the primary energy obtained from fossil fuels, whereas such energy may be used directly for heating purposes in the distillation processes. In electrodialysis electrical energy is used for the actual transfer of ions from the feed to the concentrated solution. Since the current required for the desalination process in electrodialysis is directly proportional to the number of ions that must be removed from the feed solution the energy consumption increases with increasing feed solution concentration, and at very high feed solution salt concentration electrodialysis becomes uneconomic. In electrodialysis, only ionic components are removed from a feed stream and the product water may still contain particles, bacteria, viruses, and other pollutants which must be removed in a post-treatment procedure when the product is used as potable water. Plant capacity may also play a role in total cost. While in distillation processes a substantial cost reduction can usually be achieved with an increase in the plant capacity, the scale-up factor has a relatively smaller effect in reverse osmosis.

For surface water purification and waste water treatment membrane processes such as micro- and ultrafiltration compete with flocculation, sand bed filtration, carbon adsorption, ion-exchange, and biological treatment. Here, however, membrane processes such as reverse osmosis or ultra- and microfiltration give the higher quality product water, since all other dissolved and dispersed feed water constituents can be removed and the permeate, that is, the product is more or less free of all pollutants.

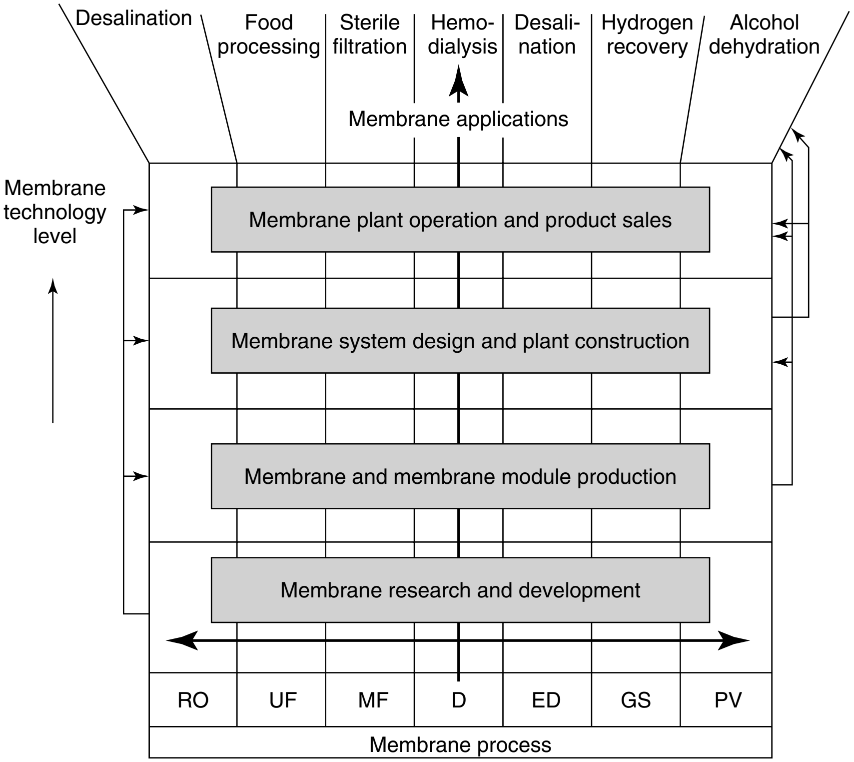
Taking all cost-affecting parameters into account, reverse osmosis seems to have a significant cost advantage over competing processes in both sea and brackish water desalination. Electrodialysis and reverse osmosis have a clear technical and economic advantage over the distillation processes. The same is true for the desalting and purification of surface water for domestic and industrial use. Here, reverse osmosis and ultrafiltration are more and more used to complement conventional processes. However, the above assessment of water purification processes is oversimplified and must be considered as a general rule with many exceptions.

The environmental impact of all membrane processes is relatively low since there are no hazardous chemicals used in the processes that have to be discharged, and there is no heat generation as has been pointed out earlier. The only effluent in desalination by reverse osmosis is a concentrated brine solution. In sea water desalination this brine causes little problems since it can be discharged directly into the sea. However, in brackish water desalination the discharge of the concentrated brine can cause problems so that brine post-treatment procedures might be necessary. Also, in surface water treatment further processing of the concentrated effluent might be necessary.

A disadvantage of membrane processes is that for many applications, especially in the chemical and petrochemical industry, their long-term reliability is not yet proven. Furthermore, membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization and membrane fouling caused by chemical interaction with water constituents. Furthermore, membranes are mechanically not very robust and can be destroyed by a malfunction in the operating procedure. However, significant progress has been made in recent years, especially in reverse osmosis sea water desalination, in developing membranes which not only have significantly better overall performance but which also show better chemical and thermal stability and are less sensitive to operational errors.

1.4
The Membrane-Based Industry: Its Structure and Markets

Parallel to the development of membrane products and processes, a membrane-based industry developed. Today, this industry has sales of several billion US$ per year and is growing steadily. Membranes and membrane processes include a large number of different products and processes with an even larger number of applications. The membrane-based industry is just as heterogeneous as membrane structures and their applications; their markets are characterized by a few rather large market segments, such as sea and brackish water desalination or hemodialysis, and a large number of small market segments in the food and chemical industries, in analytical laboratories, and in the treatment of industrial waste water streams. Several companies have concentrated on the production of membranes or membrane modules only. They offer a range of membrane products as flat sheets, hollow fibers, or capillaries with different properties for different processes and applications ranging from sea water desalination and waste and surface water treatment by reverse osmosis or ultra- and microfiltration, to fuel cell separators and medical devices, to an end user or an equipment manufacturer. Other companies manufacture membrane devices or complete systems. These companies buy the membranes or modules as key components from one or several membrane manufacturers, design and build the actual plant and very often also operate it, guaranteeing the customer a certain amount of product of a given quality. These companies generally provide a solution to the customer's separation needs which might be a combination of separation processes such as ion-exchange, carbon adsorption, flocculation and precipitation, or various chemical and biological treatment procedures in addition to membrane processes. Although the sale of membranes and membrane modules to any one of these companies is often not very large they are of importance in the membrane industry because of their specific application know-how in different markets. Finally, there are companies that provide the membranes, the system design, and the plant operation. These companies very often concentrate on a single, usually very large application such as potable water production from sea or brackish water or hemodialysis. They often not only provide the tools for producing potable water, in the case of sea water desalination, they also operate the plant and distribute the water. The larger markets are dominated by a relatively small number of large companies. A multitude of small companies are active in market niches providing service to industrial sectors. Since the market for membranes and membrane processes is rapidly growing and continuously changing there is a substantial fluctuation in the industry characterized by mergers and acquisitions.



RO reverse osmosis, UF ultrafiltration, MF microfiltration, D dialysis, ED electrodialysis, GS gas separation, PV pervaporation

Figure 1.1 The structure of the membrane-based industry, indicating the various levels of technology for various membrane processes, from research and development to applications, and the different market strategies of companies.

The structure of the membrane industry is illustrated in the schematic diagram of Figure 1.1 which shows a selected number of membrane processes and the different technology levels which can be distinguished during the development of a membrane process from basic research to the final application.

Research and development of membranes and membrane processes are the basis of all further developments and therefore indicated as the first technology level. The research is carried out mainly in academic institutions or in large companies. It requires close cooperation between various scientific disciplines such as material science and physical chemistry. It also requires the input of life science and process engineering to define the research needs concerning membrane development. The results serve as a basis for the following technology levels.

The second level in membrane technology is the production of membranes and membrane modules. Membrane producers are frequently divisions of major chemical companies. In general, these companies focus on a series of membrane products to be used in certain applications such as water desalination and purification, gas separation, bio-production, or in hemodialysis. Flat sheet membranes are mainly installed in spiral-wound modules and used mainly in water desalination and purification. Hollow fiber membrane modules are mainly used in gas separation. Plate-and-frame or tubular modules are used mainly in the chemical and food processing industry and in treating certain waste waters. Capillary type membrane modules dominate the hemodialysis market but are also applied in ultrafiltration and the production of ultrapure water.

The membranes and membrane modules produced are the key components for the membrane plant manufacturers which represent the next technology level. The number of companies involved in the design and manufacturing of membrane systems is very large and heterogeneous. Most of these companies specialize in certain applications such as the production of potable and industrial process water or the treatment and recycling of waste water streams or on the use of membranes in various industrial sectors such as the food and chemical industry. Some of the system manufacturers specialize in biomedical and laboratory devices. The system design and construction is dominated by process engineering but requires the cooperation with scientists from other scientific disciplines, such as life science, food and chemical technology, or environmental engineering which can provide the necessary application know-how for the successful use of membranes and membrane processes in a certain area.

The last level that can be identified in membrane technology is plant operation. This level is closely related to the system design and construction and to the end user of membranes and membrane processes. Engineers operating membrane plants not only need some basic knowledge of membrane research, membrane production, and membrane plant design, but also of membrane applications which often require a combination of different processes. For instance, in the production of industrial water of a certain quality a whole series of different techniques such as ion-exchange, carbon adsorption, flocculation and precipitation, or various chemical and biological treatment procedures may be applied in addition to a membrane process. In this application the membrane is just a commercially available item which must be integrated in the overall process to obtain a certain product or solve a given problem.

An assessment of the membrane-based industry indicates that companies follow two rather different approaches to the membrane market. Some companies concentrate on one technology level such as membrane production or plant construction and operation only. But they apply different membranes and different membrane processes in different applications. This is indicated by the horizontal line in Figure 1.1 for the production of membranes and modules. Other companies follow the second approach to the market which is indicated by the vertical line shown in the diagram of Figure 1.1. These companies concentrate on one process and one application only. They have their own research activities, membrane and module production, and plant design and operation, and focus on one large market which is big enough to generate the adequate profit to support a relatively large organization involved in membrane research, manufacturing, and marketing. Typical membrane applications with a large market are sea water desalination or hemodialysis. On the water market several companies have adapted the so-called build, own, operate, transport (BOOT) strategy. They no longer sell membranes or membrane plants but water which they supply to the end user. Hemodialysis companies not only build and sell artificial kidneys today but also operate dialysis stations in hospitals.

Between these extreme approaches to the membrane market there is a large number of mostly smaller companies that are active in two or more technology levels with several membrane processes and in different applications. The membrane market is still rapidly developing and changing and so is the membrane-based industry.

1.5
Future Developments in Membrane Science and Technology

In many applications today's membranes and processes are quite satisfactory, while in other new emerging or potential applications there is a substantial need for further improvements of both membranes and processes. For sea water and brackish water desalination by reverse osmosis, there are membranes available today that are quite satisfactory as far as flux and salt rejection are concerned, and the processes are proven by many years of operating experience. The same is true for hemodialysis and hemofiltration. In these applications only marginal improvements can be expected in the near future. In micro- and ultrafiltration or electrodialysis the situation is similar; the properties of present membranes are satisfactory. Nevertheless new polymer membranes with higher fluxes, higher selectivity, and better chemical and thermal stability for reverse osmosis and ultra- and microfiltration will probably be developed. Ceramic membranes with the same transport properties as polymer membranes will most likely be commercially available at competitive costs in the very near future. Ion-exchange membranes with lower electric resistance and better permselectivity will become available at significantly lower production costs. However, there are other components in the membrane processes such as the process design, application know-how, and long-term operating experience which are also of importance. In many applications of micro- and ultrafiltration, concentration polarization and membrane fouling play a dominant role, and new membrane modules and process design concepts, which provide better control of membrane fouling resulting in a longer useful life of the membranes, are highly desirable and will probably be developed using new spacer and turbulent promoter concepts. As far as the different processes are concerned, reverse osmosis will probably be more extensively applied in the food and drug industry and in the treatment of industrial effluents. Ultrafiltration has found a multitude of applications in the treatment of industrial effluents, in the food and chemical industry, and in biotechnology to separate, concentrate, and purify molecular mixtures. These applications will certainly be extended into new areas such as the treatment of municipal drinking water obtained from surface waters. The use of membrane bioreactors treating industrial and municipal waste water will probably increase significantly because fresh water sources are decreasing. Microfiltration is presently used mainly as a depth filter to remove particles or bacteria and viruses from water used in the pharmaceutical and electronic industry and in analytical laboratories. These applications are growing steadily and are being extended into new areas. In the future, cross-flow microfiltration with asymmetrically structured membranes, which would have a significantly longer useful life under operating conditions than a depth filter, will also be used to treat surface water and effluents that have much higher loads of solid materials. A very important role in the future of microfiltration will be played by ceramic membranes. Because of their good mechanical and chemical stability, they can easily be cleaned by back-flushing aggressive chemicals such as strong acids or bases or oxidizing media. Production costs of these membranes will most likely be reduced when the market for their application is increasing. The growth of electrodialysis in brackish water desalination will decrease in the future due to increasing competition from nanofiltration. However, its relevance in the treatment of industrial effluents generated by galvanic processes or in the production of pulp and paper as well as its application in the chemical and food processing industry and in biotechnology will most likely increase. Thus, in the state-of-the-art membrane processes, a steady growth can be expected in the near and midterm future with further improved membrane products and processes.

With emerging membrane processes such as gas and vapor separation and the use of membrane contactors and catalytic membrane reactors the membrane-based industry will most likely grow significantly in the years to come. Especially in the treatment of natural gas and in applications in the petrochemical industry there are many opportunities for the application of membrane processes when membrane structures with the required properties become available. At this point it should be mentioned that gas diffusion based on Knudsen diffusion at elevated temperature in ceramic porous membranes has been used since the middle of the last century for the enrichment of uranium as fuel for nuclear reactors. The market for catalytic membrane reactors is very large but also very heterogeneous and requires in addition to the proper membranes, a significant amount of specific application know-how. The same is true for membrane contactors and integrated membrane processes. Here, process development is a key factor for success, but for the near and midterm future these processes should have a substantial growth potential. For other processes such as facilitated transport with fixed and mobile carriers and the production of acids and bases by electrodialysis with bipolar membranes future development will be more difficult to estimate, since no real large markets for these processes have been developed so far because of the shortcomings of membranes available today.

With their intrinsic properties of high energy efficiency, high transport selectivity, large operational flexibility and environment compatibility, membranes and processes are important tools for advanced molecular separations and chemical transformations overcoming the limits of the traditional industrial processes. In spite of the fact that the membranes and membrane processes of today have a significant technical and commercial impact there are still substantial research and development needs for the development of more efficient membranes and membrane processes, as well as for new applications. Especially in the biomedical area membranes can play an important role that goes far beyond their present use in the artificial kidney and blood oxygenation. As key components in hybrid artificial organs membranes may be able to support or substitute functions of biological membranes. In these applications new membranes with specific transport properties and high transport rates must be developed. An indication as to what membranes are capable of doing in biomedical applications can be obtained by taking a closer look at the structure and functions of biological membranes in living organisms.

1.5.1
Biological Membranes

The structure and function of a biological membrane is illustrated in Figures 1.2–1.4. Figure 1.2 shows a simplified schematic drawing of a so-called lipid bilayer which represents the basic structure of a biological membrane, which separates the cell from its surrounding and controls the exchange of mass energy and electrical charges in a very specific way.

The structure of a biological membrane contains lipid molecules which have a hydrophobic and a hydrophilic part being arranged in such a way that the hydrophilic part is directed to the aqueous medium at the membrane surface while the hydrophobic part is directed toward the inside of the membrane. The entire membrane is about 10 nm thick and permeable to relatively small molecules which are soluble in a hydrophilic as well as in a hydrophobic environment such as certain gases. Larger molecules and hydrophilic components such as certain salt ions are unable to penetrate the hydrophobic part of the membrane. The transport of hydrophilic components such as certain ions is achieved by large proteins which are integrated in the bilayer membrane in such a way that they penetrate the entire membrane and form a channel that provides a transport for certain components.

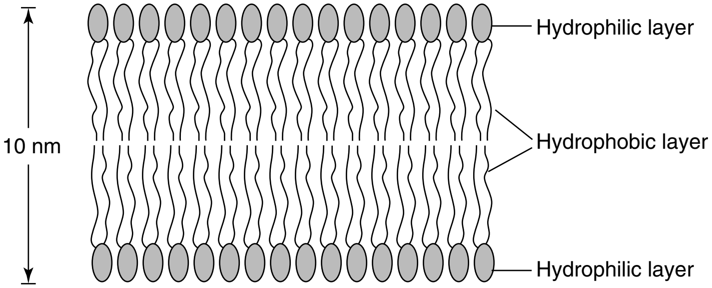


Figure 1.2 The structure of a biological lipid bilayer membrane.

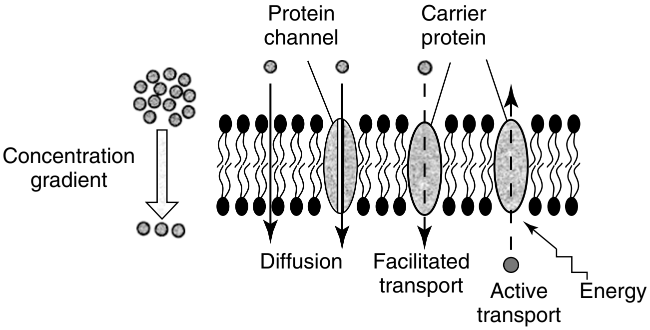


Figure 1.3 The different transport properties of biological membranes.

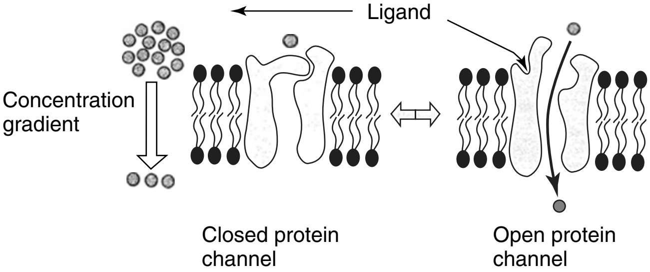


Figure 1.4 Gated biological membranes with ligand-controlled transport properties.

This transport can be very specific for selected components only, due to the driving force of a chemical potential gradient across the membrane. Transport through the membrane protein can also be against the chemical potential gradient, where the energy for the transport is provided by a chemical reaction within the membrane protein. This form of transport is referred to as *active transport*. The different modes of transport in biological membranes are illustrated in Figure 1.3 which shows a simplified schematic drawing of a biological membrane indicating the transport of molecules through the lipid bilayer phase and through a protein channel due to diffusion initiated by a concentration difference between the two phases separated by the membrane. In addition other protein channels provide facilitated transport in which certain components are transported specifically by so-called carrier molecules. Furthermore, there are still other protein channels in which certain components are transported against their electrochemical potential gradient which is also referred to as *active transport*.

Another interesting structure found in biological membranes is the so-called *gated* membrane in which the mass transport is controlled by the presence of certain components which can open a protein channel in a lipid bilayer. A gated membrane and its function is illustrated in the schematic drawing of Figure 1.4 which shows a lipid bilayer membrane with a protein channel. Transport through this channel protein is controlled by a ligand which can open the channel by a specific interaction with the protein.

In reality biological membranes are much more versatile and complex as the schematic drawings of Figures 1.2–1.4 indicate. Nevertheless biological membranes can provide a guideline to possible future developments of synthetic membranes and their biomedical applications.

1.6
Summary

Because there are many very different membrane structures and membrane processes, having highly diversified applications, the development of new membranes and membrane processes requires very close cooperation between the various scientific disciplines. Membrane development requires a basic knowledge of material science and of physical chemistry. The development and optimization of membrane processes require a basic knowledge of process engineering and process modeling. The application of membranes often requires special know how of life science, chemical and biochemical, or environmental engineering.

The literature of membrane science and technology is just as diverse as membrane properties and their applications. Various aspects of membranes and their application are described in a large number of reference books and scientific journals. To obtain a relatively comprehensive understanding of presently used membranes and membrane processes and possible future developments, a large number of books and journals must be studied. A few recently published books are listed below. It must, however, be realized that this list represents only a very small portion of the available books on membrane science and technology, and that the selection is arbitrary and does necessarily list the most relevant books.

Recommended Reading

1. General introduction to membrane science

Baker, R.W. (2004) *Membrane Technology and Applications*, John Wiley & Sons, Ltd, Chichester, UK.

Ho, W.S. and Sirkar, K.K. (1992) *Membrane Handbook*, Van Nostrand Reinhold, New York, USA.

Mulder, M. (1996) *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, The Netherlands.

2. Membrane process development and applications

Drioli, E. and Giorno, L. (2009) *Membrane Operations*, Wiley-VCH Verlag GmbH, Weinheim, Germany.

Noble, R.D. and Stern, S.A. (eds) (1995) *Membrane Separation Technology, Principles and Application*, Elsevier, Amsterdam, The Netherlands.

Pabby, A.K., Rizvi, S.S.H., and Sastre, A.M. (2009) *Handbook of Membrane Separations*, CRC Press, Boca Raton, USA.

3. Membrane preparation

Burggraaf, A.J. and Cot, L. (1995) *Fundamentals of Inorganic Membrane Science and Technology*, Elsevier, Amsterdam, The Netherlands.

Lloyd, D.R. (ed.) (1985) *Material Science of Synthetic Membranes*, ACS Symposium Series, vol. 269, American Chemical Society, Washington, DC, USA.

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