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SUMMARY

In this chapter an introduction is given to today's state of the art of membrane science and technology. The chapter begins with the definition of terms and provides a general description of technically relevant membrane structures and membrane processes that are used today in separation processes, in energy conversion, and in the controlled release of active agents. The advantages as well as the limitations of membrane processes in mass separation are indicated. Major applications of membranes are described and their technical and commercial relevance pointed out. A short overview over the historical development of membrane science and technology is given and possible future developments and research needs are indicated.
1.1 General considerations

Synthetic membranes are widely used today in many technically and commercially relevant separation processes including sea and brackish water desalination, purification bioproducts and food stuff, and the separation of gases and vapors. They are also key components in energy conversion and storage systems, in artificial organs and drug delivery devices. This large-scale application of membranes, however, is relatively recent although the first studies on membranes date back more than 250 years when in 1748 Nollet discovered the effect of osmotic pressure. With the beginning of the 20th century the first man-made membranes with controlled pore sizes became available and around the middle of this century membranes evolved to become a major tool in water desalination and purification, stimulated by the increasing needs of adequate quality water for domestic and industrial use.

Sea and brackish water desalination has been one of the first large-scale applications of membranes. But it is not only an important application for membranes, it also has stimulated the development of other membrane processes such as micro- and ultrafiltration and especially hemodialysis which have equal or higher commercial relevance today. Recently, processes such as gas separation, pervaporation and membranes in medical devices or energy storage and conversion systems are becoming more and more important.

Although synthetic membranes are widely used as valuable scientific and technical tools in a modern industrialized society they are not very well defined in the mind of the public. The most prominent association that many people have when thinking of a membrane resembles that of a filter, i.e. just a device capable of separating various components from a liquid mixture according to their size or chemical nature.

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 resistivity can vary from millions of ohm-cm to a fraction of an ohm-cm. Another characteristic property of a membrane is that its permeability for various components can be very different, i.e. some membranes are "semipermeable". 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 electric field. The permeability of a membrane for various components is determined by the structure of the membrane and the size of permeating
components as well as by the chemical nature and electrical charge of the membrane material and permeating components. The transport of certain components through a membrane may be facilitated by certain chemical compounds, coupled to the transport of other components, or activated by a chemical reaction occurring in the membrane. These phenomena are referred to as facilitated, coupled, or active 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 two different regions and controls the exchange of matter, energy, and information between the regions in a very specific way.

We can distinguish between biological membranes, which are part of the living organism, and synthetic membranes that are man-made. Biological membranes carry out very complex and specific transport tasks in our bodies. They accomplish them quickly, efficiently, and with minimal energy expenditure, frequently using active transport. Synthetic membranes are not nearly as complicated in their structure or function as biological membranes. They have only passive transport properties and are usually less selective and energy efficient. In general, however, they have significantly higher chemical and mechanical stability, especially at elevated temperature. The selectivity of synthetic membranes is determined by a sieving or by a solution-diffusion mechanism, i.e. components are transported through a microporous structure according to their size or through a homogeneous structure according to their solubility and diffusivity. 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. Some driving forces such as concentration, pressure, or temperature gradients act equally on 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- and ultrafiltration, dialysis, electrodialysis, Donnan dialysis, pervaporation, gas separation, etc.

Even more heterogeneous than membrane structures and membrane processes are their practical applications. The large-scale industrial utilization of membranes began about 1970 with the production of potable and industrial water. Since then they have become widely used in many applications such as in the biomedical area, the separation of gases, and the treatment of industrial effluents just to mention a few commercially relevant operations. Because membranes
are capable of separating molecular mixtures very selectively and efficiently at room temperature by physical means their potential applications are extremely wide. There are three main areas of application of membranes and membrane processes: In the first area are applications where the use of membranes is technically feasible, but there are other processes with which membranes must compete on the basis of overall economy. This, for instance, is the case in seawater desalination and the treatment of certain waste-water streams. Here membranes must contend with distillation and biological treatment, respectively. In the second area alternative techniques are available, but membranes offer a clear technical and commercial advantage. This is the case in brackish water desalination and the production of ultra-pure water. Then there are applications where there is no reasonable alternative to membrane processes. This occurs in certain drug delivery systems or with artificial organs. Today the membrane-based industry is growing more than 10% per year. However, with the development of new membranes having better chemical, thermal, and mechanical properties or are capable of providing more selective and energy efficient carrier-facilitated transport, the use of membrane processes will most likely extend far beyond its present level.

1.2 Historical development of membranes and membrane processes
Although membranes have existed and functioned in nature as long as life has existed on earth, there are no references to them or to their function until the beginning of the eighteenth century. A systematic study of synthetic membranes began as recently as 100 years ago and the first practical utilization of membranes dates back only 50 years. Thus the history of membrane science and technology is relatively short. Nevertheless, we can distinguish three periods, i.e. the early study of membrane phenomena, the first preparation of synthetic membranes and the large-scale industrial production and utilization of membranes.

1.2.1 Early studies of membrane phenomena
The first recorded study of membrane phenomena and the discovery of osmosis dates back to Nollet (1748). He discovered quite accidentally that when a pig's bladder was brought in contact on one side with a water-ethanol mixture and on the other side with pure water, the latter would pass preferentially.
Nollet was probably the first to recognize the relation between a semipermeable membrane, osmotic pressure, and volume flux. It is, however, not clear whether the term osmosis, which originally was associated with mass transport through membranes due to the metabolic activities of living cells, was also introduced by him. Originally, the term osmosis described the passage of both water and solutes. The latter was called exosmosis by Dutrochet in 1827 in contrast to endosmosis which described the transport of water only. The term electroosmosis was introduced even earlier by Porret who observed that an electric current flowing through a diaphragm can cause a transport of water. More systematic studies on mass transport in semipermeable membranes were carried out by Graham (1833). He studied the diffusion of gases through different media and discovered that rubber exhibits different permeabilities to different gases. He also developed a simple membrane dialyser and used it to separate a solution into its components. The work of Graham stimulated Mitchell to study gas and liquid permeation through various materials including animal intestines and natural elastic materials. He found, as did Nollet, that a membrane made from pig's bladder transports water preferentially and also that a membrane made from an elastomer transports ethanol preferentially when either membrane is in contact with a water-ethanol mixture.

Most of the early studies on membrane permeation were carried out with natural materials such as animal intestines, bladders or gum elastics. Traube in 1867 was the first to introduce an artificially prepared semipermeable membrane by precipitating cupric ferrocyanide in a thin layer of porous porcelain. This type of membrane was used by Pfeffer in his fundamental studies on osmosis. However, the theoretical treatment and much of the interpretation of osmotic phenomena and mass transport through membranes is based on the studies of Fick in 1877 who interpreted diffusion in liquids as a function of concentration gradients, and that of van t'Hoff (1887) who gave a thermodynamic explanation for the fact that the osmotic pressure of dilute solutions is directly proportional to the concentration of individual particles in the solution. Little later Nernst in 1889 and Planck in 1890 introduced the flux equation for electrolytes under the driving force of a concentration or electrical potential gradient. The first publications on electrodialysis with neutral membranes were those of Morse and Pierce in 1903. With the classical publications of Donnan (1911), describing the theory of membrane equilibria and membrane potentials in the presence of non-dialyzing electrolytes, the early history of membrane
science ends with most of the basic phenomena satisfactorily described and theoretically interpreted.

1.2.2 The first preparation of synthetic membranes and their application
With the beginning of the twentieth century membrane science and technology entered a new phase. First of all Bechhold (1908) developed a method of making the first synthetic membranes as we usually think of them 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. The importance of swelling for membrane permeability was recognized in 1926 by Kahlenberg. He also found that the permselectivity of a membrane is determined not only by solute size but also by its chemical nature, i.e. its solubility in the membrane matrix. Control of membrane permeability was achieved by dissolving dry nitrocellulose in various alcohol-water mixtures. The alcohol in this casting solution not only caused a substantial swelling of the subsequently-made film but also dissolved and thus removed low molecular fractions of nitrocellulose from the film, thus considerably increasing its permeability for low molecular weight components. Membranes with a wide range of swelling, i.e. porosity, were prepared by Eggert in 1921, who was the first to use a phase inversion process to prepare membranes from a solution of nitrocellulose in ethanol-ether mixture by precipitation in water. Nitrocellulose membranes were also used in the studies of Zsigmondy and Bachmann (1918) as ultrafilters to separate macromolecules and ultrafine particles from an aqueous solution. These studies were later continued by many others, including Manegold in 1929, Elford in 1930, and McBain and Kistler in 1931.

Between 1930 and the second world war the interest in membranes and membrane processes increased dramatically. The transport through liquid (oil) membranes was discussed in a 1932 published paper by Osterhout and Stanley. Diffusion coefficients of ions and low molecular weight components in agar gels were determined in 1930 by Friedman and Kramer. The relation between the streaming potential, which is obtained when a liquid is forced through a porous diaphragm, and the applied hydrostatic pressure was developed by Bull in a 1935 published paper. Electroosmosis and electrodialysis are also treated in a 1931 published monograph of Prausnitz and Reitstötter. At about the same time Meyer and Sievers and T. Teorell developed independently their model for transport through ion-selective charged membranes. This model
became the basis for the understanding of electrodialysis as well as membrane electrodes. In 1938 the phenomena related to osmosis were treated in very great detail by Schreinemakers. The state of the art of membrane science was discussed in a 1937 Faraday Society workshop on biological and synthetic membranes with important contributions by Meyer, Manegold, Mitchel, and many others. During the same year the first ultra- and microfiltration membranes became commercially available. Based on a 1922 patent of Zsigmondy, Sartorius GmbH in Germany began in 1937 the production of a series of nitrocellulose membranes with various pore sizes. These membranes were sold to microbiological laboratories in small quantities mainly for analytical applications. During the second world war membrane research almost ceased for more than five years. Nevertheless a few significant developments were made during this time, the most important one being the development of the first successfully functioning hemodialyser by Kolff and Berk (1944). All synthetic membranes available up to that time were micro-porous structures separating mixtures exclusively according to their size.

1.2.3 Recent history of membrane science
After the second world war membrane science and technology entered a new phase. Until then membranes had been mainly a subject of scientific interest with only a very 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. The work was stimulated by several important events. First, progress in polymer chemistry resulted in a large number of synthetic polymers which ultimately became available for the preparation of new membranes with specific transport properties plus excellent mechanical and thermal stability. Second, the previously developed thermodynamics of irreversible processes proved a very useful tool to describe mass transport in various membrane processes. Starting with Onsager (1931) a comprehensive theory was developed. Since processes in biological as well as in synthetic membranes are generally irreversible it seemed logical to apply the thermodynamics of irreversible processes to describe membrane transport properties. A few of the papers that have influenced the theoretical treatment of membrane processes substantially include those of Staverman (1951), Kedem and Katchalsky (1961), Schlögl, and Spiegler.
A second route for describing membrane processes was based on postulating certain membrane transport models, such as the model of a pore membrane, by Schmidt in 1950, the charged pore model by Meyer and Sievers in 1936 and that of a diffusion-solution membrane by Merten (1966). The properties of ion-exchange membranes were studied extensively by Meares in 1957, Helfferich in 1962 and many others by using membrane models as well as the above-mentioned rigorous treatment based on the thermodynamics of irreversible processes.

While the theoretical treatment of membrane phenomena certainly was an important step in the development of membrane technology, it was the need for an energy efficient and economic process for the production of potable water from sea and brackish water sources that triggered the large scale development of membranes with the desired properties and led to the growth of a substantial membrane-based industry. Reid recognized this potential in reverse osmosis. Supported in the late 1950s by the Office of Saline Water, US-Department of the Interior, Reid and Breton (1959) found that some polymer films, in particular cellulose acetate, showed rather good retention for salts under reverse osmosis conditions. Unfortunately, the permeation rate per unit area, i.e. the permeate flux, was disappointingly low.

Unaware of Reid’s work, Sourirajan independently discovered the good salt retention of cellulose acetate membranes in reverse osmosis tests and, like Reid, obtained very low fluxes. This flaw was overcome with the discovery of the anisotropic cellulose acetate membrane by Loeb and Sourirajan (1962). This membrane provided high salt rejection and high fluxes at moderate hydrostatic pressures, a major advance toward the application of reverse osmosis membranes as an effective tool for the production of potable water from the sea. It was later shown by Kesting (1971) that the process of making anisotropic membranes, which were then generally referred to as asymmetric skin-type membranes, is a phase inversion process in which a homogeneous polymer solution is converted into a two phase system, i.e. a solid polymer rich phase providing the solid polymer structure and a polymer lean phase forming the liquid filled membrane pores. Strathmann, Kock, Amar and Baker (1971) rationalized the formation of asymmetric membranes and correlated different structures with the various preparation parameters. It was shown that the phase inversion process of making anisotropic structures could be applied to any polymer that is soluble in an appropriate solvent at a given temperature and will precipitate by addition of a non-solvent at certain conditions of temperature and concentration. Soon other synthetic polymers such as polyamides, polyacrylonitrile,
polysulphone, polyethylene, etc. were used as basic material for the preparation of synthetic membranes. These polymers often showed better mechanical strength, chemical stability, 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 interfacially-polymerized composite membrane by Cadotte and independently Riley as reported by Cadotte and Petersen (1980). These membranes showed significantly higher fluxes and rejection than the cellulose acetate membranes and were less sensitive to high pH-values. These qualities were largely due to the fact that with composite membranes the skin, which determines the membrane selectivity and flux, is added to an existing porous substructure which only provides the support for the skin and has little effect on flux and rejection of the membrane, hence each phase can be chosen to satisfy its function.

A different approach to membrane geometry was taken in the early 1960s by Mahon (1966). He made self-supporting hollow fiber membranes which had a wall thickness of only 6 to 7 microns. Nevertheless, the permeate flux was rather low, presumably because the fibers were isotropic in structure. This problem was overcome later by the Du Pont Corporation, which made an asymmetric hollow fiber membrane.

Soon after the development of efficient membranes, appropriate membrane housing assemblies, called modules, were devised. The criteria for the design of such modules included high membrane packing density (the ratio of membrane area to module volume), reliability, ease of membrane or module replacement, control of concentration polarization, and low cost. Membranes were produced in three different configurations, i.e. as flat sheets, as hollow fine fibers and as tubes. The first municipal reverse osmosis plant, installed at Caolinga, California by the University of California, Los Angeles, California in 1965, used tubular modules, which have a 1:1 ratio of membrane surface to pressurized vessel surface and had a packing density of 140 m² per m³. Today's’ reverse osmosis desalination plants all use spiral wound modules or hollow fiber membrane modules which are higher in packing density by one or two orders of magnitude, respectively. Westmoreland and Bray (1982) pioneered the spiral wound module. The hollow fiber membrane module was developed by Du Pont.

Basic studies on mass transfer were carried out at the Massachusetts Institute of Technology by Sherwood and others (1965), Oak Ridge National Laboratory, and other organizations, public and private. Except for the University of California, which was supported by the state, most
developments in the USA were funded by the Office of Saline Water, the main driving force there for the development of the membrane-based industry. However, there were also developments funded entirely by industry such as the polyamide hollow fiber membranes of DuPont which are highly competitive with the cellulose acetate and composite sheet membranes used today in spiral wound modules.

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 work of Meyer and Strauss who developed the first multicell stack just before the second world war. However, modern electrodialysis became a practical reality with the work of Juda and McRae (1953) who developed the first reliable ion-exchange membranes having both good electrolyte conductivity and ion-permselectivity. Electrodialysis was first commercially exploited for the desalination of brackish water by Ionics Inc., which in the early 1950s sold the first plants to Saudi Arabia. The commercial success of Ionics was due to their membranes, their compact stacking and the mode of operation referred to as electrodialysis reversal (Katz 1979), which provided a periodic self-cleaning mechanism for the membrane stack and thus allowed long-term continuous operation at high concentrations of scaling materials.

While Ionics pioneered the development of electrodialysis and dominated the market in the USA there were many others who contributed substantially to the growth of electrodialysis technology. These included research institutions in The Netherlands, Israel, South Africa, Russia, China, and especially Japan, where a completely different use of electrodialysis was envisaged. Here electrodialysis was used for concentrating sodium chloride solutions from seawater to produce table salts as described by Nishiwaki. In this application a low electrical resistance of the membrane was of prime importance for the economics of the process. These requirements have led to the development of membranes with very low electrical resistance though at the cost of some mechanical strength.

With the introduction of electrodialysis into the food and drug industry, and especially into the treatment of certain industrial effluents, further improvements of both the cell system design and the membranes became necessary. In the early 1980s a completely new area for application of electrodialysis was opened up. At this time K.J. Liu et al. (1976) introduced bipolar membranes for the recovery of acids and bases from the corresponding salts by electrical potential-induced water dissociation.
Ever since reverse osmosis has been used successfully for the desalination of brackish water a substantial effort has been also concentrated on the development of efficient reverse osmosis membranes for seawater desalination. Progress has been slower than desired. However, spin-off products of this effort, such as microfiltration, ultrafiltration and especially hemodialysis membranes used in the artificial kidney very quickly led to a membrane-based industry with annual sales of membrane products which exceed those of reverse osmosis seawater desalination membranes by an order of magnitude.

The development of the hemodialyser is based on the early work of Kolff et al. in 1944. It has been predominantly a European affair, stimulated by the nationalized medicare. Any person suffering from acute or chronicle renal failure had the right to the best therapy, which was then and still is hemodialysis. This led to a very rapid development of an advanced hemodialyser-producing industry. Since the artificial kidney is a disposable item, which has to last only a few hours, very large quantities of membranes must be manufactured at very low cost. Based on a large and very predictable market, companies in The Netherlands, Sweden, and Germany soon dominated a membrane market valued at more than US $ 1.5 billion in 1998. Other medical applications such as blood oxygenation, controlled release of drugs, or diagnostic devices are a significant part of the overall membrane market.

Another development that has stimulated the membrane-based industry is the need for high quality industrial water. The production of high-density integrated circuits requires ultrapure water. Also in other industries and in analytical and microbiological laboratories there was and still is a need for high quality water that could be efficiently produced by membrane processes using reverse osmosis and microfiltration membranes as point-of-use filters. Thus the largest markets for membranes are today in microfiltration and hemodialysis.

In the near future, surface water treatment might well become just as important as sea and brackish water desalination today. With a steady deterioration of potable water quality due to contamination of water sources by municipal, industrial and agricultural effluents, there is a need for efficient and economic treatment techniques for both effluent streams and unacceptable drinking water, and here again membranes will most probably play an important role.

The large-scale separation of gases and vapors is also a relevant industrial area for membrane applications. Gas separation was pioneered by Henis and Tripodi in 1981. Originally, the aim 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 CO₂ from natural gas or
the recovery of organic vapors from off-gases and the separation isomers are typical applications
for gas and vapor separation. In contrast to gas separation, which today is an important industrial
process, the use of pervaporation on a large industrial scale has not been realized. Pervaporation
has a number of interesting potential applications. But so far very few large commercial plants
have been built.

1.2.4 Key developments in membrane technology

Emerging new technologies are often characterized by key discoveries providing a breakthrough
by their application. This is also true in membrane science and technology. The understanding of
membrane properties developed continuously from the early experiments on biological materials
to the mathematical description of the osmotic and mass transport phenomena by the
thermodynamics of irreversible processes. For the large-scale application of membranes, the
preparation by Zsigmondi in 1922 of the first synthetic membranes with a wide and adaptable
porosity range was a significant step. The seminal discovery for reverse osmosis was the
anisotropic concept achieved with asymmetric cellulose acetate membranes by Loeb and
Sourirajan (1962). The expansion of this concept by Cadotte and Petersen (1981), who made the
first really efficient composite membranes, was another breakthrough in reverse osmosis
membrane development. The spiral wound module of Westmoreland and Bray enabled compact
packing of other sheet membranes. The DuPont Corporation successfully developed and
marketed an asymmetric hollow fiber membrane and a module for containing it. Because of the
small fiber diameter the module packing density is very high, considerably exceeding that of the
spiral-wound module.

In electrodialysis the development of a multi-cell arrangement in the stack between electrodes by
Meyer and Strauss (1940) was a significant step towards practical application. Equally important
for the success of electrodialysis was the introduction of the electrodialysis reversal concept as
described by Katz (1979).

There are many more key developments that had a significant effect on the development of
membrane technology such as the preparation of the first efficient ion-exchange membranes by
Juda and McRae (1953) and the first tailor-made ultrafiltration membranes by Michaels and
Baker in 1968. A real breakthrough in the medical application of membranes was the first
successful hemodialysis treatment of patients suffering from renal failure by Kolff and Berk (1944). The first electron micrographs of the asymmetric cellulose acetate reverse osmosis membranes by Riley (1966) and the description of the membrane structure formation as a phase inversion process by Kesting were important steps for optimizing membrane structures and properties. The development of gas separation is closely related to the work of Henis and Tripodi (1989), and the basics of pervaporation were studied by Aptel and Neel (1968). The use of the first bipolar membranes by Liu, Chlanda, and Nagasubramanian in 1977 must also be included. Parallel to the development of membranes and membrane processes was that of the membrane-based industry. These developments were spearheaded by pioneers. Some of these pioneers became a commercial success, while others disappeared or were taken over by other larger enterprises.

1.3. Advantages and limitations of membrane processes

In water desalination and purification the membrane processes compete directly with the more conventional water treatment techniques. However, compared to these conventional procedures membrane processes are very energy efficient, simple to operate and yield a high quality product. For the desalination of brackish water either reverse osmosis or electrodialysis can be used. They are in direct competition to distillation which, however, has significantly higher energy consumption and is affected by scaling and fouling. In this application both electrodialysis and reverse osmosis seem to have substantial cost advantages. In seawater desalination, reverse osmosis is the only cost effective membrane process today and is competing directly with distillation. Depending on local conditions, including water quality, energy cost and the required capacity of the desalination plant, either distillation or reverse osmosis can be the more efficient process. For very large capacity units and if a power plant can be coupled with the desalination unit, distillation is generally considered to be more economical. For small and medium size capacity units reverse osmosis is generally preferred. For surface water purification and wastewater treatment membrane processes, especially micro- and ultrafiltration, are competing with flocculation, sand bed filtration, carbon adsorption, ion-exchange and biological treatment. The membrane processes are usually more costly but generally provide a better product water quality.
Very often a combination of conventional water treatment procedures with membrane processes results in reliable and cost-effective treatment combined with high product water quality. The major disadvantage of membrane processes is that until today the long-term reliability is not completely proven. Membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization, chemical interaction with water constituents, and fouling. Membranes are mechanically not very robust and can easily be destroyed by a malfunction in the operating procedure. However, significant progress has been made in recent years, especially in reverse osmosis seawater 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. Practical experience gained by the nations in the Middle East has resulted in more reliable operation.

1.4 Cost considerations and environmental impact

All membrane processes are quite energy efficient. This general statement, however, has to be examined in more detail. Water treatment cost depends very much on the membrane process, its application, and the competing technology according to Leitner (1968). For micro- and ultrafiltration the energy requirements for the actual filtration process are indeed quite low. However, in many applications such as surface water treatment or waste-water treatment micro- and ultrafiltration are competing with biological treatment or sand bed filtration which need even less energy. In sea-water desalination the only economical membrane process is reverse osmosis which is competing with the various distillation techniques. As far as energy consumption is concerned, reverse osmosis is the more energy efficient process. However, it has to be taken into account that 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 in electrodialysis increases with increasing feed solution concentration. There are, however, other factors determining the overall economics of a process such as the investment and operating costs or various pre- and post-
treatment procedures of the feed solution and the product water. Plant capacity may also play a role in total cost. While in distillation processes usually a substantial cost reduction can be achieved with an increase in the plant capacity, the scale-up factor has a relatively smaller effect in reverse osmosis. In general, reverse osmosis seems to have a slight cost advantage over competing processes in seawater desalination. In desalination of brackish water, both 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, however, reverse osmosis gives the higher-quality product water. In reverse osmosis not only salts but also all other dissolved and dispersed feed water constituents are retained by the membrane and the permeate, i.e. the product is more or less free of all pollutants. In electrodialysis, only ionic components are removed from a feed stream and the product water may still contain particles, bacteria, viruses, and other pollutants. It should be understood, however, that the above classification of water purification processes is very general and may be oversimplified. Depending on the feed water composition and the required product water quality, a combination of processes might be appropriate. For example, if ultra-pure water for certain industrial applications is required, a sequence of processes may be applied, such as reverse osmosis with microfiltration as a “point-of-use-filter” to remove traces of particles, and ion-exchange techniques to remove all ions. Often microfiltration is also used in combination with reverse osmosis as a pretreatment procedure.

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

Pressure-driven membrane processes do not cause any health hazard. The product obtained is generally of high quality. Thus, very little post-treatment procedures are required. Sometimes chlorination may be applied to guarantee the required sterility of potable water, especially when longtime storage is required in a hot climate.
1.5 The membrane based industry

The structure of the membrane-based industry is quite heterogeneous even when only one typical application such as the desalination and purification of water is considered. One type of company has focused its efforts on the manufacturing of membranes and membrane modules. It very often offers a range of membrane products with different properties for different feed and product water requirements. It is, however, not involved in the construction of systems and actual desalination plants. A second type is the system manufacturer. 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 water of a given quality. Sometimes, these companies provide different processes, such as reverse osmosis, nanofiltration or electrodialysis according to the requirements of the feed water and desired product water. Finally, there are companies that provide the membranes, the system design, and the plant operation. Since the market for membranes and water supply systems is rapidly growing and continuously changing there is a substantial fluctuation in the industry characterized by mergers and acquisitions. Presently, the market is dominated by a relative small number of large companies serving rather large market segments, such as the supply of potable water, and by a multitude of smaller companies active in market niches such as treating certain waste water streams or providing ultra pure water for the electronic industry.

With a steadily growing world population and increasing industrialization of our society the demand for potable and industrial water of sufficient quality has increased drastically. In many areas of the world the natural fresh water sources are unable to meet the demand, neither in quantity nor in quality, and extensive water management is required which includes both treatment of water sources usually not considered to be suited as potable water because of high salinity and the recycling of certain industrial and municipal waste water streams. In the arid zones of the world water desalination and especially seawater desalination plays an important role. Modern technology provides a whole series of techniques for the treatment of saline as well as polluted surface water or industrial and municipal effluents. These techniques include distillation, ion-exchange, carbon adsorption, filtration and flocculation, and various biological treatment procedures. Some of the more promising techniques for the treatment of both fresh and
waste-water are based on membrane processes. Depending on the water composition microfiltration, ultrafiltration or, for saline solutions such as sea and brackish water, reverse osmosis and electrodialysis can be applied.

1.5.1 Membrane and membrane module producers
Membrane producers are frequently divisions of major chemical companies that manufacture hollow fiber, tubular, capillary, or flat sheet membranes. In general, these companies focus on certain processes or applications such as reverse osmosis and sea or brackish water desalination, or on microfiltration and the treatment of industrial effluents or hemodialysis. In most cases the company which produces the membranes also produces the appropriate modules. Flat sheet membranes are mainly installed in spiral wound modules and used mainly in sea and brackish water desalination. The same is true for hollow fiber membrane modules. Both module types provide a rather large membrane area per unit volume and have similar investment cost for a given plant capacity, but also require a substantial amount of pretreatment. For seawater desalination hollow fiber and spiral wound modules have about equal market shares while in brackish and surface water treatment the spiral wound module seems to dominate. 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 ultra-pure water.

The basic materials and the actual manufacturing process that different companies use for their membranes and modules also vary. Some companies produce asymmetric membrane structures for reverse osmosis and nano- and ultrafiltration from cellulose esters or polyamides. Other companies are manufacturing composite membranes with a porous polysulfone support structure and a polyamide type barrier layer made by interfacial polymerization.

1.5.2 System manufacturers
The number of companies involved in the design and manufacturing of membrane water treatment systems is very large and heterogeneous. Most of these companies are specialized on certain applications, such as the production of potable water or industrial process water or the treatment and recycling of waste water streams from the food, the chemical, and pharmaceutical or the metal processing industry. Some of these enterprises are quite small, and membrane
processes may play only a minor role in their overall business activity. Their overall business activity may be focused on water treatment in general for a certain application and include generally a whole series of different techniques, such as ion-exchange, carbon adsorption, flocculation and precipitation, or various chemical and biological treatment procedures. For these companies the membrane is just a commercially available item with specific desired properties. Although the sales of membranes and membrane modules to anyone 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. Exceptions to this rule are major utility companies that provide membranes, modules, and systems as a complete package. In general, these companies have secured their membrane supply by acquiring small or medium size membrane manufacturers.

There are, however, especially in electrodialysis, membrane manufacturers that also provide systems and sell water in a certain guaranteed quality as their end product. In this case the membrane production, the system manufacturing, and the plant operation are all in one hand.

1.6 The membrane market development

The membrane market is characterized by a few rather large market segments, such as sea and brackish water desalination, the production of ultrapure water, or hemodialysis and a large number of small market segments in the food, chemical, and pharmaceutical industries, analytical laboratories and especially in the treatment and recycling of industrial waste water streams. It is rather difficult to make a reasonably accurate forecast about the future developments of the market for membranes. However, due to the fact that the demand for potable and industrial water of adequate quality is increasing drastically and that the sources of fresh water with the required quality are steadily decreasing worldwide, there will be a need for energy-efficient and affordable processes for the production of high quality water from sea and brackish water sources as well as from waste or polluted surface waters. Since membrane processes have proven to be amongst the most energy efficient and economic means for this purpose it is quite likely that for the foreseeable future the membrane water purification industry will continue to grow. The growth will also depend on further developments of membranes with improved selectivity and higher fluxes as well as better chemical, thermal, and mechanical stability. Long-term experience with their application in large plants will also contribute to
increase the useful life of the membranes, thus making the processes more reliable and economical.

1.7 Conclusions and outlook
Synthetic membranes and membrane processes for water desalination and purification first became commercially available about a quarter of a century ago. Since then they have developed from laboratory tools to industrial products and processes with significant technical and commercial relevance. Membrane science and technology has reached a state of development such that for many applications today’s membranes and processes are quite satisfactory while in other applications there is a definite demand for further improvements of both the membranes and the processes.

For sea and brackish water desalination by reverse osmosis, e.g. there are membranes available today that are quite satisfactory as far as flux and salt rejection are concerned. There is, however, a definite need for improving their long-term chemical, thermal, and mechanical properties. None of the commercially available reverse osmosis membranes can be operated for a long period at pH-values below 4 or above 8 and at temperatures in excess of 40°C. For the treatment and recycling of industrial effluents chemical stability is of critical concern not only during operation but also during cleaning cycles.

In micro- and ultrafiltration or electrodialysis the situation is similar. The properties of present membranes are satisfactory but steady improvements of membrane properties can be expected. Revolutionary developments, however, are more unlikely in these areas. While the properties of the available membranes are of critical concern, there are other components such as the membrane module, the process design, application know-how and long-term operating experience that are just as important. For reverse osmosis and electrodialysis in sea and brackish water desalination both the membrane modules and process design are proven by many years of operating experience, and thus can be regarded as mature technologies for this application. In micro- and ultrafiltration applications related to surface water or industrial effluent treatment the situation is quite different. Here, concentration polarization and membrane fouling play a dominant role and new membrane modules and process design concepts which provide a better control of membrane fouling resulting in a longer useful life of the membranes would be highly desirable. In other membrane processes such as gas separation, pervaporation, fuel cell
separators, membrane reactors, etc. the situation is quite different. Here, better membranes, improved process design and extensive application know-how and long-term experience are mandatory to establish membrane processes as a proven and reliable technology.

1.8 References


2 Fundamental aspects of membranes and membrane processes

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SUMMARY

In this chapter the common fundamentals of different membrane processes are described. In the first part a general description of the different membrane structures, such as porous and homogeneous or symmetric and asymmetric structures, and their function is given. The main terms used in membrane processes, such as membrane permeability, membrane permselectivity and membrane rejection, are defined. The basic thermodynamic relations relevant for the description of mass transport phenomena in membranes and membrane processes are treated and the mathematical relations used to describe the mass transport in membranes and in the different membrane processes are derived. Finally, the energy requirements in membrane separation processes are discussed.
2.1 General Considerations

Membrane processes such as dialysis, electrodialysis, reverse osmosis or micro- and ultrafiltration differ widely as far as the applied membrane structures and the driving forces for the actual mass transport are concerned. There are, however, some common fundamentals, such as certain thermodynamic and kinetic relations describing the mass transport in membranes and at the membrane/bulk solution interface. Phenomena such as concentration polarization and membrane fouling occur in all membrane processes and have common causes and consequences. Thus, before treating the different membrane processes and their application in more detail some common fundamentals will be discussed.

2.2 Definition of a membrane and its function

A precise and complete definition of a membrane that covers all its aspects is rather difficult, even when the discussion is limited to synthetic structures as in this outline. In the most general sense, a synthetic membrane is an interphase that separates two phases and restricts the transport of various components in a specific manner (Lonsdale 1989). A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure. It may be solid or liquid and may consist of organic or inorganic materials. It may be neutral or it may carry positive or negative charges, or functional groups with specific binding or complexing abilities. Its thickness can be less than 100 nm to more than a millimeter. The electrical resistance may vary from more than 1,000,000 ohm cm² to less than one ohm cm². The term "membrane", therefore, includes a great variety of materials and structures, and a membrane can often be better described by its function rather than by its structure. Some materials, such as protective coatings, or packaging materials, though not meant to be membranes, show typical membrane properties, and are in fact membranes. All materials functioning as membranes have one characteristic property in common: They restrict the passage of different components in a very specific manner. Separation of a mixture in a membrane process is the result of different transport rates of different components through the membrane. The transport rate of a component through a membrane is determined by driving forces such as concentration, pressure, temperature and electrical potential gradients and the concentration and mobility of the component in the membrane matrix. Membrane processes can be grouped according to the applied driving forces into pressure driven processes such as reverse osmosis or ultra- and microfiltration,
concentration gradient driven processes such as dialysis and Donnan dialysis, and in electrical potential driven processes such as electrodialysis.

The mechanism by which certain components are transported through a membrane can also be very different. In some membranes, for example, the so-called solution-diffusion types the transport is based on the solution and diffusion of individual molecules in the membrane matrix. In other membranes the transport is based on viscous flow through individual pores.

2.3 Materials and structures of synthetic membranes

Synthetic membranes show a large variety in their physical structure, the materials they are made from, and in their function. They can be classified in four basic groups: (1) porous films, (2) homogeneous solid films, (3) barriers carrying electrical charges, and (4) liquid or solid films containing selective carriers. Furthermore, membranes come in two typical structural configurations: their structure can be symmetric or asymmetric, independent of whether they are homogeneous solid films, microporous media or electrically charged barriers. In asymmetric membranes structural aspects such as homogeneous films and porous media are often combined. The materials used for the preparation of membranes can be polymer ceramics, glass, metals and liquids. The schematic drawing of Figure 2.1 illustrates the morphology and materials of some technically relevant synthetic membranes. The figure shows the cross-sections of symmetric structured membranes consisting of a homogeneous film, a porous medium with cylindrical pores and a porous medium with a sponge-like structure and also the cross-section of asymmetric structures consisting of a porous medium with increasing pore sizes from top to bottom and two structures with a homogeneous film on an asymmetric porous support structure. In one case the film is an integral part of the membrane and in the other case the membrane consists of a composite structure with the film made from a different material than the support structure.
2.3.1 Symmetric and asymmetric membranes

As indicated earlier synthetic membranes may have a symmetric or an asymmetric structure. In a symmetric membrane the structure and the transport properties are identical over the entire cross-section and the thickness of the entire membrane determines its flux. Symmetric membranes are used today mainly in dialysis, electrodialysis and microfiltration. In asymmetric membranes structural as well as transport properties vary over the membrane cross-section. Most of the membranes used today in pressure driven separation processes are composed of rather sophisticated asymmetric structures in which the two basic properties required of any membrane, i.e. high mass transport rates for certain components and good mechanical strength, are separated. An asymmetric membrane consists of a very thin (0.1 to 1 μm) "skin" layer on a highly porous 100 to 200 μm thick substructure. The thin skin on top of the asymmetric porous structure represents the actual selective membrane. Its separation characteristics are determined by the nature of the membrane material or the pore size of the skin-layer. Its mass flux is
determined mainly by the "skin" thickness. The porous sub-layer serves only as a support for the mostly very thin and fragile skin and has little effect on the separation characteristics or the mass transfer rate of the membrane. Asymmetric membranes are used primarily in pressure driven membrane processes such as reverse osmosis, ultrafiltration, or gas and vapor separation, since here the unique properties of asymmetric membranes, i.e. high fluxes and good mechanical stability can best be utilized. Two techniques are used to prepare asymmetric membranes: one utilizes the phase inversion process which leads to an integral structure with the skin and the support structure made from the same material in a single process (Kesting 1971), and the other resembles a composite structure where a thin barrier layer is deposited on a microporous substructure in a two step process (Cadotte 1985). In this case barrier and support structures are generally made from different materials.

2.3.2 Porous membranes
A porous structure represents a very simple form of a membrane, which closely resembles the conventional fiber filter as far as the mode of separation is concerned. These membranes consist of a solid matrix with defined holes or pores which have diameters ranging from less than 1 nm to more than 10 µm. Separation of the various components is achieved strictly by a sieving mechanism with the pore diameters and the particle sizes being the determining parameters. Porous membranes can be made from various materials such as ceramics, graphite, metal or metal oxides, and various polymers. Their structure may be symmetric, i.e. the pore diameters do not vary over the membrane cross-section, or they can be asymmetric, i.e. the pore diameters increase from one side of the membrane to the other typically by a factor of 10 to 1000. The techniques for the preparation of porous membranes can be rather different and include simple sinter processes, irradiation, and etching techniques as well as phase inversion and polymer precipitation procedures. Porous membranes are used to separate components that differ markedly in size or molecular weight in processes such as micro- and ultrafiltration or dialysis (Cheryan 1998).

2.3.3 Homogeneous membranes
A homogeneous membrane is merely a dense film through which a mixture of molecules is transported by a pressure, concentration, or electrical potential gradient. The separation of the
various components of a mixture is directly related to their transport rates within the membrane phase, which is determined mainly by their diffusivities and concentrations in the membrane matrix. Homogeneous membranes are referred to as solution-diffusion type membranes (Merten 1965). An important property of these membranes is that chemical species of similar sizes, and hence similar diffusivities, may be separated efficiently when their concentration, which is determined by their solubility in the membrane phase, differs significantly. Homogeneous membranes are prepared from polymers or in some cases from metals and metal alloys by various film-forming techniques. Since the mass transport in homogeneous membranes occurs strictly by diffusion their permeabilities are rather low. Homogeneous membranes are used mainly to separate components which are similar in size but have different chemical nature in processes such as reverse osmosis, gas and vapor separation, and pervaporation (Raymond et al. 1992). In these processes asymmetric membrane structures are used which consist of a thin homogeneous skin supported by a porous substructure.

2.3.4 Ion-exchange membranes
Films carrying charged groups are referred to as ion-exchange membranes, consist of highly swollen gels carrying fixed positive or negative charges. The properties and preparation procedures of ion-exchange membranes are closely related to those of ion-exchange resins (Helfferich 1961). As with resins, there are many different polymers that provide the membrane matrixes and different functional groups to confer the ion-exchange properties.
There are two different types of ion-exchange membranes: (1) cation-exchange membranes which contain negatively charged groups fixed to the polymer matrix, and (2) anion-exchange membranes which contain positively charged groups fixed to the polymer matrix. In a cation-exchange membrane, the fixed anions are in electrical equilibrium with mobile cations in the interstices of the polymer. In contrast, the mobile anions are more or less completely excluded from the cation-exchange membrane because of their electrical charge which is identical to that of the fixed ions. Due to this exclusion of the anions, a cation-exchange membrane permits transfer of cations only. Anion-exchange membranes carry positive charges fixed on the polymer matrix. Therefore, they exclude all cations and are permeable to anions only. Although there are a number of inorganic ion-exchange materials, most of them based on zeolites and bentonites, these materials are rather unimportant in ion-exchange membranes compared to polymer
The main application of ion-exchange membranes is in electrodialysis, electrolysis, batteries, fuel cells, and more recently also in pervaporation (Strathmann 1995).

2.3.5 Liquid membranes
Liquid membranes have gained increasing significance in recent years in combination with the so-called facilitated transport which utilizes "carriers" which transport certain components such as metal-ions selectively and at a relatively high rate across the liquid membrane interphase. Generally, it is no problem to form a thin fluid film. It is difficult, however, to maintain and control this film and its properties during a mass separation process. In order to avoid a break-up of the film, some type of reinforcement is necessary to support such a weak membrane structure. Two different techniques are used today for the preparation of liquid membranes. In the first case, the selective liquid barrier material is stabilized as a thin film by a surfactant in an emulsion-type mixture (Li et al.1981). In the second technique a porous structure is filled with the liquid membrane phase. Both types of membranes are used today on a pilot-plant stage for the selective removal of heavy metal ions or certain organic solvents from industrial waste streams (Kemperman et al. 1998). They have also been used rather effectively for the separation of oxygen and nitrogen.

2.3.6 Fixed carrier membranes
Closely related to both liquid membranes with mobile carriers and ion-exchange membranes with fixed negative or positive charges are the so-called fixed carrier membranes. These membranes consist of a homogeneous or porous structure with functional groups which selectively transport certain chemical compounds. Fixed carrier membranes can have a symmetric or asymmetric structure depending on their application. They are used today, e.g. in co- and counter-current transport and in separation of oxygen and nitrogen or alkane/alkene mixtures.

2.4 Fluxes and driving forces in membrane separation processes
Separation in membrane processes is the result of differences in the transport rates of different chemical species through the membrane. The transport rate is determined by the driving force or forces acting on the individual components and their mobility and concentration in the
membrane. The mobility of a component in the membrane is primarily determined by its size and the physical structure of the membrane material while the concentration of the solute in the membrane is primarily determined by the chemical compatibility of the permeating component and the membrane material. In membrane separation processes there are different forms of mass transport as indicated in Figure 2.2, which show schematically the mass transport through membranes separating two homogeneous phases.
general form of mass transport through a membrane

carrier facilitated transport

flux coupled transport

co-current flux coupling

counter-current flux coupling

coupling force is the electroneutrality requirement
In the most general form the Flux through a membrane can be described by:

\[ J = -p \frac{dX}{dz} \]  \hspace{1cm} (2.1)

Here \( J \) is a flux, \( P \) is phenomenological coefficient expressing the permeability of the membrane and \( \frac{dX}{dz} \) is the driving force.

The flux through the membrane can be expressed as:

1. Volume flux  \( J_v \) expressed in volume per time, e.g. \( \text{m}^3 \text{s}^{-1} \)
2. Mass flux  \( J_m \) expressed in mass per time, e.g. \( \text{kg m}^{-2} \text{s}^{-1} \)
3. Molar flux  \( J_n \) expressed in mole per time, i.e. \( \text{mol m}^{-2} \text{s}^{-1} \)
4. Electrical flux  \( J_e \) expressed in Faraday per time, i.e. \( \text{A m}^2 \)
5. Heat flux  \( J_q \) expressed in heat per time, e.g. \( \text{J m}^{-2} \text{s}^{-1} \)

The different fluxes can be converted into each other:

\[ J_v = J_m \rho^{-1} = J_n M^{-1} = J_e C^{-1} z^{-1} F^{-1} = J_q C^{-1} C_p^{-1} \]  \hspace{1cm} (2.2)

Here \( \rho \) is the density (\( \text{kg m}^{-3} \)), \( M \) is the molecular weight (\( \text{kg mole}^{-1} \)), \( F \) is the Faraday constant (\( \text{A s mole}^{-1} \)), \( z \) is the valence of an ion, i.e. the electrical charges per ion, \( C \) is the concentration (\( \text{mole m}^{-3} \)), and \( C_p \) is the heat capacity (\( \text{J mole}^{-1} \))

The different fluxes are conventionally described by simple linear relations between the flux and the driving force, such as:

Fouries law  \[ J_q = -\alpha \frac{dT}{dz} \]  \hspace{1cm} (2.3)
Fick's law  \[ J_n = -D \frac{dC}{dz} \]  \hspace{1cm} (2.4)

Darcy's law  \[ J_v = -L_p \frac{dp}{dz} \]  \hspace{1cm} (2.5)

Ohm's law  \[ J_e = \kappa \frac{d\phi}{dz} \]  \hspace{1cm} (2.6)

Here \( T \) is the temperature, \( C \) is the concentration, \( p \) is the pressure, \( \phi \) is the electrical potential, \( \alpha \) is the heat transfer coefficient, \( D \) is the diffusion coefficient, \( L_p \) is the hydrodynamic permeability and \( \kappa \) is the electric conductivity.

The driving force for the transport of a component \( A \) from a phase (') to a phase (") through a membrane \( \frac{dX}{dz} \) can be expressed as a gradient in its concentration, its temperature, its electrical potential, and its pressure. The concentration and the electrical potential of a component are expressed by its chemical or electrochemical potential \( \mu_A \), \( \eta_A \) respectively where the electrochemical potential is given by:

\[ \eta_A = \mu_A + z_A F \phi \]  \hspace{1cm} (2.7)

Here \( \phi \) and \( z_A \) are the electrical potential and the valence of the component \( A \), and \( F \) is the Faraday constant.

Generally, temperature gradients have little effect on mass transport in membranes and can, therefore, in technically relevant membrane processes be neglected.

In conclusion, the membrane acts as a barrier through which all components are transported under the driving force of a gradient in their electrochemical potential or in hydrostatic pressure. Gradients in the electrochemical potential of a component in the membrane interphase may be caused by hydrostatic pressure, concentration, temperature, or electrical potential differences between the two phases separated by the membrane. Depending on the driving force and the transport mechanism in the membrane three different forms of transport are distinguished:
1. diffusion of a component $i$, with $\text{grad } \mu_i$ being the driving force,
2. migration of a charged component with $\text{grad } \phi$ being the driving force and
3. convection of a volume with $\text{grad } p$ being the driving force. In many membrane processes all three forms of mass transport are found. It should be noted that the gradient of the chemical or electrochemical potential always refers to the membrane phase. It is usually assumed that the membrane phase is in equilibrium with the adjacent outside phases, i.e. the electrochemical potentials in the membrane $\eta^m$ and in the adjacent phase $\eta'$ are identical. This, however, is not true for the concentration of a component which is usually very different. As a matter of fact, the concentration differences of a component in the membrane and the adjacent phase is often the main parameter determining the membrane separation capability. Thus, when Fick's law is applied to describe the diffusion through a membrane the concentration in the membrane phase has to be considered. This concentration is related to the outside phase by:

$$C^m = k C'$$  \hspace{1cm} (28)

where $k$ is a distribution coefficient which is, e.g. in homogeneous polymer membranes, identical with the solubility coefficient.

**Carrier facilitated transport**

In many cases the membrane is just a physical barrier without specific interactions between the permeating components and the membrane matrix. In other cases permeating species can have specific interactions with certain "carrier" components in the membrane which enhance the membrane permeability for these species. The so-called carrier facilitated transport is also shown schematically in Figure 2.2. The driving force for the transport of the various components is again the gradient in their electrochemical potential across the membrane. The transport of the different components, however, is facilitated by specific carriers which are confined to the membrane phase. There are two types of membranes with carrier facilitated transport properties. The first type is a membrane with the carriers fixed to the membrane matrix where the transported component moves through the membrane by "hopping" from one carrier to the next (Cussler 1991). The second type is a liquid membrane with the mobile carrier dissolved in a liquid film. Here, the transported components are coupled to the carrier on one side of the
membrane, i.e. the side facing the feed solution. Then they are transported through the membrane coupled to the carrier by diffusion. On the other side of the membrane, i.e. the side facing the permeate, the transported components are released and the carrier diffuses back to the feed side of the membrane. Liquid membranes consist either of a surfactant stabilized liquid film or of a solid porous structure with the pores filled with the liquid membrane material. Carrier facilitated transport is, however, more selective than diffusion through a membrane that acts merely as physical barrier without specific interactions between the permeating components and the membrane material. The transport of various components through a membrane may also be achieved by a coupling of solute fluxes as also indicated in Figure 2.2. In flux coupled transport two forms of coupling can be distinguished. One is referred to as co-current coupled transport and the other is referred to as counter-current coupled transport. Flux coupled transport, e.g. can be obtained when electrically charged components have different permeability in a membrane. Here, the coupling of fluxes is the result of the electroneutrality condition which requires that on a macroscopic scale there is no excess of electrical charges. Thus, positively or negatively charged components can only be transported across a membrane when the same number of opposite charges are transported in the same direction or if the components with the same charges are transported in the opposite direction. In an ion containing system electroneutrality must always prevail. The co-current transport is of little technical relevance today. The counter-current transport which is usually referred to as Donnan dialysis is used in water softening and the treatment of certain waste waters. It will be discussed in more detail later.

*Interdependence of fluxes and driving forces*

Transport processes are conventionally described by well known equations which relate the fluxes of various components to the corresponding driving forces in the form of linear relations. Fick's law, for example, describes the relation between the flux of individual components and a concentration gradient. Ohm's law describes the relation between an electrical current and an electrical potential gradient. Fourier's law describes the relation between heat transport and a temperature gradient and Darcy's law describes the relation between a volume flux and a hydrostatic pressure difference. In membrane processes, driving forces and fluxes may be interdependent, giving rise to new effects. Thus, a concentration gradient across a membrane may not only result in a flux of matter but, under certain conditions, can also cause the build-up
of a hydrostatic pressure difference. This phenomenon is referred to as osmosis. Similarly, a
gradient in hydrostatic pressure may not only lead to volume flux, but may also result in the
formation of a concentration gradient. This phenomenon is called reverse osmosis. A
temperature gradient across a membrane may not only result in a flux of heat, but can lead to a
transport of matter, a phenomenon referred to as thermo-osmosis. The complexity of the
interaction of fluxes and driving forces is illustrated in Figure 2.3.

Fig. 2.3  Schematic diagram illustrating the relation between fluxes and driving forces in
membrane separation processes (\(\Delta T\), \(\Delta a\), \(\Delta p\), and \(\Delta \phi\) refer to differences in temperature, activity,
pressure, and electrical potential, respectively; \(\alpha\), \(D\), \(L_p\), and \(\kappa\) refer to heat transfer and diffusion
coefficient, hydraulic permeability, and resistance)

In membrane processes there are four major driving forces, i.e., temperature, activity, electrical
potential, and hydrostatic pressure gradients. The fluxes directly related to these driving forces,
often referred to as "corresponding" fluxes, are indicated in Figure 2.3 by vertical lines. Thus, a
temperature gradient leads directly to a flux of heat, an activity gradient to a flux of individual
molecules, an electrical potential gradient to an electrical current and a hydrostatic pressure
gradient to a volume flux. The horizontal lines in Figure 2.3 indicate the direct interaction of
driving forces expressed in the streaming potential, diffusion potential or the Dufour effect. The diagonal lines connect the driving forces with the not directly related fluxes, e.g., an activity gradient leading to a volume flux is referred to as osmosis and a hydrostatic pressure difference resulting in a flux of individual molecules is called reverse osmosis. If an electrical potential difference leads to fluxes of individual components or a volume this phenomenon is referred to as electrodialysis or electroosmosis, etc. There may also be a kinetic coupling of individual components resulting in a flux of other components. One example of the coupling of fluxes is the transport of bound water with an ion which is transported across a membrane by an electrical potential gradient. In a mathematical treatment of membrane transport processes, the kinetic coupling of individual components, however, can often be neglected (Hase 1963). For technically and commercially relevant membrane separation processes and their practical application, only driving forces which can lead to a significant flux of matter are of practical importance. These driving forces are a) hydrostatic pressure, b) concentration, or c) electrical potential differences.

a) A difference in hydrostatic pressure between two phases separated by a membrane can lead to a momentum flux of a bulk solution and to a separation of chemical components when the hydrodynamic permeability of the membrane is different for different components;

b) A difference in the concentration of various components in two phases separated by a membrane can lead to transport of matter and separation of the various components when their diffusivities and/or concentrations in the membrane are different;

c) A difference in the electrical potential between two phases separated by a membrane can lead to transport of matter and separation of various chemical components when differently charged particles show different mobilities in the membrane.

*Membrane separation property*

In most technically relevant applications the capability of a membrane to separate different components from each other, i.e. the membrane permselectivity is the most important membrane property. This separation capability can be expressed by a selectivity or a rejection factor. The membrane selectivity is given by:
Here is $S_{A,B}^P$ the permselectivity of a membrane for the components A and B, and $P_A$ and $P_B$ are their permeability. $R_A$ is the rejection of the component A by the membrane, $C_A'$ and $C_A''$ are the concentrations of the component A in the two phases separated by the membrane, for instance, a feed solution and a filtrate when a filtration process is considered.

2.4.1 Basic thermodynamic relations with relevance in membrane processes

Transport of heat, mass, electrical charges, and individual components between two systems separated by a semipermeable membrane will occur only when the systems are not in equilibrium, i.e. when the two systems are in different thermodynamic states. The state of a system is determined by a number of state parameters describing the extensive and intensive properties of the system. Extensive properties are the mass, the volume, and the total energy of a system. Extensive properties depend on the size of the system under consideration. They are additive and the total quantity consists of the sum of its parts. Intensive properties such as temperature, pressure or molar properties are independent of the size of the system. The relation between the different state parameters are described by the state functions such as the Gibbs free energy (Atkins 1994) which is given by:

$$G = U + pV - TS \quad \text{(2.11)}$$

Here $G$ is the free enthalpy also referred to as the Gibbs energy or Gibbs free energy. $U$ is the internal energy, $p$ the pressure, $V$ the volume, $T$ the temperature, and $S$ the entropy of the system under consideration.
Changes in a system are described by the differential of the state function. For a closed system, which has no exchange of matter with the surrounding, changes in the system are given by:

\[ dG = dU + pdV + Vdp - TdS - SdT \]  

(2.12)

According to the first law of thermodynamics, i.e. the conservation of energy, changes in the internal energy \( U \) of a system are the result of energy transferred to the system in form of heat or work done on the system and given by:

\[ \Delta U = q + w \]  

(2.13)

Here \( \Delta U \) is the change of the internal energy of a system, \( q \) is the heat transferred to the system, and \( w \) the work done on the system.

For infinitesimal changes of the state of the system the change in the internal energy can be expressed by:

\[ dU = dq + dw \]  

(2.14)

If assumed that the work done on the system consists of expansion work at constant pressure, i.e. \( dw = pdV \), Equation (2.14) can be written as:

\[ dU = dq - pdV \]  

(2.15)

The entropy of a system and its change is expressed by the second law of thermodynamics which states that in isolated systems the entropy change is zero for reversible and positive for irreversible, i.e. spontaneous processes. Thus, when heat is exchanged reversibly with the surrounding the entropy change in the system is given by:

\[ dS = \frac{dq_{rev}}{T} \]  

(2.16)
Introducing Equations (2.15) and (2.16) into (2.12) gives the change in the Gibbs free energy for a reversible process:
\[ dG = Vdp - SdT \quad (2.17) \]

For constant temperature and pressure and for reversible processes is:
\[ (dG)_{p,T} = 0 \quad (2.18) \]

Equation (2.18) shows that for reversible processes at constant temperature and pressure the Gibbs free energy is at a minimum and the entropy production zero.

The entropy change in a system with heat being transferred from the surrounding to a system can be broken down in two parts, i.e. a part which is given by the heat transferred from the surrounding to the system denoted as \( \Delta_{\text{tr}}S \) and a part that is produced in the system as the result of a spontaneous change \( \Delta_iS \):
\[ dS = \Delta_{\text{tr}}S + \Delta_iS \quad (2.19) \]

The entropy production \( \Delta_iS \) is zero for reversible processes and positive for irreversible processes.
\[ \frac{\Delta_iS}{dt} \geq 0 \quad (2.20) \]

For isothermal spontaneous processes, i.e. irreversible processes, the change in the Gibb's free energy is positive. It is a measure for the irreversibility of a process and referred to as the so-called dissipation function given by:
\[ -\left( \frac{dG}{dt} \right)_{p,T} = T \frac{\Delta_iS}{dt} \quad (2.21) \]

The dissipation function expressed in Equation (2.21) describes the changes of the Gibb's free energy in a closed system, i.e. without an exchange of matter. For an open system, i.e. any
process involving mass transfer into or out of the system an additional contribution to the total Gibb's free energy has to be taken into account. For an open system the change of the Gibb's free energy is given by:

\[ dG_{p,T} = \sum_i \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j} \, dn_i = \sum_i \mu_i dn_i \quad i = 1, 2, 3, \ldots, n \; ; \; i \neq j \] (2.22)

Here \( dG_{p,T} \) is the total Gibb's free energy change of an open system at constant pressure and temperature, and \( n_i \) is the number of moles of the component \( i \); \( \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j} \) is the partial molar Gibb's free energy. It is referred to as the chemical potential of the component \( i \) denoted by \( \mu_i \) in a system that contains neutral components only. If a component is electrically charged its chemical potential must be replaced by the electrochemical potential as will be discussed in more detail later.

It should be noted that the partial molar Gibb's free energy, i.e. the chemical potential \( \mu_i \) is an intensive property while the total Gibb's free energy is an extensive property. The extensive property is the summation of its partial molar properties. This holds true for all other state variables, too. Thus is:

\[ \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_j} = \bar{V}_i \quad \text{and} \quad \left( \frac{\partial S}{\partial n_i} \right)_{p,T,n_j} = \bar{S}_i \] (2.23)

Furthermore is:

\[ V = \sum_i n_i \bar{V}_i, \quad S = \sum_i n_i \bar{S}_i \quad \text{and} \quad G = \sum_i n_i \mu_i \] (2.24)

Here \( \bar{V}_i \) is the partial molar volume, and \( \bar{S}_i \) is the partial molar entropy.

The chemical potential is also a function of temperature, pressure, and composition, and its change at constant temperature can be expressed by:
\[ d\mu_i = \bar{V}_i dp + \sum_k \frac{\partial \mu_i}{\partial n_k} dn_k \quad (2.25) \]

The last term in Equation (2.25) describes the chemical potential of a component \( i \) as a function of other components in a mixture. In analogy to an ideal mixture the composition dependent part of the chemical potential can be expressed by a standard potential referring to the pure component and composition dependent term. At constant pressure and temperature the chemical potential of a component \( i \) is given by:

\[ \left( \mu_i \right)_{p,T} = \mu_i^0 + RT \ln a_i \quad (2.26) \]

Here \( \mu_i^0 \) is the chemical potential of the pure component \( i \) under standard condition of temperature and pressure, and \( a_i \) is the activity of the component \( i \) in a mixture.

The change of the chemical potential of a component \( i \) in a mixture at isothermal conditions is:

\[ d\mu_i = \bar{V}_i dp + RT d\ln a_i \quad (2.27) \]

In membrane processes there are generally two homogeneous systems separated by a membrane. The chemical potential of each component in the two systems has a defined value \( \mu_i' \) and \( \mu_i'' \).

Here the superscripts ('') and (''') refer to the two phases separated by the membrane. The number of moles \( n_i \) in each phase is changed only by the transport of a component \( i \) from one phase to the other through the membrane and therefore is:

\[ dn_i' = -dn_i'' \quad (2.28) \]

For small changes of the number of moles in the two phases the change in the Gibb's free energy, that is caused by the mass transfer between the two phases, is given by combination of Equations (2.22) and (2.28):
\[
\frac{dG}{dt} = \sum_{i} (\mu_{i} - \mu'_{i}) \ln \frac{a_{i}''}{a_{i}'} \quad (2.29)
\]

Here \( \mu_{i} \) and \( \mu'_{i} \) are the chemical potentials of the component \( i \) in the two phases separated by the membrane.

The driving force for the transport of the component \( i \) from one phase to the other is the difference in the chemical potential, \( \Delta \mu_{i} = \mu'_{i} - \mu''_{i} \).

The flow of the component \( i \) through the membrane is given by the change of the number of moles of the component \( i \) per unit time:

\[
\frac{dn_{i}''}{dt} = AJ_{i} \quad (2.30)
\]

Here \( A \) is the membrane area and \( J_{i} \) is the flux per unit area.

Introducing Equations (2.21), (2.28) and (2.29) into Equation (2.30) gives a relation for the entropy production in the total system when mass is transported from one phase to the other. At constant temperature and pressure thus is:

\[
T \frac{dS}{dt} = -\left( \frac{dG}{dt} \right)_{p,T} = \sum_{i} \left( \mu'_{i} - \mu''_{i} \right) \frac{dn_{i}'}{dt} = \sum_{i} J_{i} \Delta \mu_{i} \quad (31)
\]

For the transfer of a small amount of the component \( i \) from one phase to the other the total Gibbs free energy is unchanged and the entropy production zero representing a reversible process near to equilibrium.

As indicated in Equation (2.27), the changes in the chemical potential of a component are caused by changes in temperature, pressure, and activity.

The driving force for a component from one phase to the other is given by the difference in its chemical potential in the two phases. Thus is:

\[
\Delta \mu_{i} = \mu'_{i} - \mu''_{i} = \bar{V}_{i} \Delta p + RT \ln \frac{a''_{i}}{a'_{i}} \quad (2.32)
\]
Equation (2.32) is an important relation which not only describes the driving force for the transport of a component i from one phase to another as a function of a pressure and activity difference, it also indicates that equilibrium between the two phases for the component i can be achieved, i.e. \( \mu'_i = \mu''_i \) even if it has different activities in the two different phases when this activity difference is compensated by a pressure difference.

The chemical potential describes the partial molar Gibb's free energy for a system that contains neutral components only.

If a system contains charged components, i.e. ions, the partial molar Gibbs free energy depends also on the electrical potential and the chemical potential as expressed in Equation (2.27) is replaced by the electrochemical potential of a component:

\[
d\eta_i = \overline{V}_i dp + RT d\ln a_i + z_i F \phi
\]  

(2.33)

Here \( \eta_i \) is the electrochemical potential, \( z_i \) is the electrochemical valence of the ion i and \( \phi \) the electrical potential.

Accordingly the entropy production as expressed by Equation (2.31) for neutral components can be related to the transport of ions by:

\[
T \frac{dS}{dt} = \sum_i A J_i \Delta \eta_i
\]  

(2.34)

The activity \( a_i \) in Equation (2.33) and the flux \( J_i \) in Equation (2.34) refer to ions.

The ion concentrations in an electrolyte solution are related by the electroneutrality condition which states that the number of positive and negative charges in a macroscopic system must be equal. The electroneutrality condition for an electrolyte solution is given by:

\[
\sum_i z_i C_i = 0 = \sum_i z_i v_i C_s
\]  

(2.35)
Here \( C_i \) is the concentration, \( z_i \) is the valence of an ion \( i \), \( C_s \) is the concentration of the electrolyte, i.e. a salt or an acid or base, and \( \nu_i \) is a stoichiometric coefficient which gives the number of ions formed when one mole of an electrolyte dissociates in a solution.

For a monovalent electrolyte such as NaCl \( \nu_i \) is one for both ions. For a salt that dissociates into more than two ions such as i.e. CaCl\(_2\), \( \nu_{\text{Ca}} \) is 1 and \( \nu_{\text{Cl}} \) is 2.

2.4.2 Chemical and electrochemical equilibrium in membrane systems

Equilibrium between two systems is obtained when the systems are in the same state, i.e. when the Gibb's free energy in both systems are identical and thus no transport of mass or energy between the systems occurs. Since the Gibb's free energy of a system is a function of various state variables such as temperature, pressure, electrical potential, and the activity of individual components differences in these state variables between two systems can lead to fluxes of heat, momentum, electrical charges or individual components.

Two systems separated by a membrane which is impermeable to some components and permeable to others may well be in equilibrium, even if they do have differences in pressures, electrical potentials or the activities of individual components as long as these differences compensate each other. Examples for two systems being in equilibrium are the osmotic equilibrium in which pressure and activity differences compensate each other, and the Donnan equilibrium which is obtained when an electrical potential difference is compensated by activity difference. For membrane processes the osmotic as well as the Donnan equilibrium are of importance and will be discussed in more detail.

2.4.2.1 Osmotic equilibrium, the osmotic pressure, and forward and reverse osmosis

If two aqueous salt solutions of different concentrations are separated by a membrane which is permeable for the solvent, e.g. water, but impermeable for the solute, e.g. salt, a transport of water from the more dilute solution to the more concentrated solution is observed. This phenomenon which is illustrated in Figure 2.4 is referred to as osmosis. The figure shows a schematic diagram of a membrane separating two solutions consisting of a solvent, e.g. water, and a solute, e.g. a salt. The two solutions are indicated by (') and ("'). The membrane is assumed to be permeable to the solvent, but impermeable to the solute. Depending on the concentrations
and hydrostatic pressures in the two phases separated by the membrane four different situations can be distinguished:

a) The concentrations and the hydrostatic pressures in both solutions are equal. This situation is referred to as complete or chemical equilibrium and there will be no fluxes of matter across the membrane.

b) The hydrostatic pressures in the two phases separated by the membrane are equal but the solute concentration in solution (') is higher than the one in solution ("'). In this case the osmotic pressure in solution (') is higher than that in solution ("') and there will be a flow of solvent from the more diluted solution ("') into the more concentrated solution ('). This situation is referred to as osmosis.

c) The two phases separated by the membrane have different hydrostatic pressures, but the difference in hydrostatic pressure is equal to the difference in the osmotic pressures between the two solutions. This situation is referred to as osmotic equilibrium and there will be no flow of solvent through the membrane although the concentrations in the two solutions are different.

d) The two phases separated by the membrane have different hydrostatic pressures, but the difference in hydrostatic pressure across the membrane is larger than that in an osmotic pressure acting in opposite direction. Thus, solvent will flow through the membrane from the solution (') with the higher solute concentration into the solution ("') with the lower solute concentration. This phenomenon is referred to as reverse osmosis.
Fig. 2.4 Schematic drawing illustrating the osmotic phenomenon. (It shows two phases ('') and ("') separated by a semipermeable membrane. The phases consist of a solvent and a solute indicated by the subscripts l and s. C and \( \mu \) refer to concentration and chemical potential, p to hydrostatic and \( \pi \) to osmotic pressure, respectively, and J to the transmembrane flux.)

The flux of solvent between two homogeneous solutions of different concentrations separated by a semipermeable membrane, which is only permeable for the solvent, to the more concentrated solution as a function of an hydrostatic pressure applied is illustrated in Figure 2.5. Here, the solvent flux between two solutions of different concentrations through a strictly semipermeable membrane is shown as a function of the hydrostatic pressure applied to the more concentrated solution.

![Diagram](image)

Fig. 2.5 Solvent flux between two solutions of different concentrations through a strictly semipermeable membrane as function of the hydrostatic pressure applied to the more concentrated solution
As long as the applied hydrostatic pressure is lower than the osmotic pressure difference between the two solutions solvent will flow from the more dilute solution into the more concentrated solution by osmosis. When the hydrostatic pressure exceeds the osmotic pressure difference the flow is reversed and solvent will flow from the more concentrated solution to the dilute solution. This process is referred to as reverse osmosis.

The osmotic pressure

The osmotic pressure of a solution $\pi$ is proportional to the solute concentration $C_S$. It can be calculated from the chemical potential of the solvent considering the following experiment. A solution of a solute in a solvent is separated from the pure solvent by a strictly semipermeable membrane which is only permeable to the solvent. In most cases of practical relevance the solvent is generally water and the solvent a salt. However, in an aqueous solution salts are dissociated in two or more ions and since the osmotic pressure of the solution is determined by the total number of individual species in the solution the degree of dissociation and the stoichiometric coefficients of the salt have to be considered for determining the osmotic pressure as will be shown later. For simplicity reasons the osmotic pressure shall be derived for a single component solute. To determine the osmotic pressure of a solution consisting of a solvent and a single solute osmotic equilibrium is assumed. This means there is no flux through the membrane and the hydrostatic pressure on the solution is higher than that on the solvent and in fact equal to the osmotic pressure of the solution. Under osmotic equilibrium conditions the chemical potential of the solvent in the solution, $\mu_1^S$ is equal to that of the solvent, i.e. $\mu_1^1$. Thus:

$$\mu_1^S = \mu_1^1$$ (2.36)

The chemical potential of the solvent in the solution is:

$$\mu_1^S = \mu_1^0 + \nabla_1 p^S + RT \ln a_1^S$$ (2.37)
Here $\nabla$ is the partial molar volume of the solvent, $\mu^0$ is the chemical potential of the solvent under standard conditions of pressure and temperature, $a_l$ is the activity of the solvent, $p$ is the hydrostatic pressure, and the superscript $s$ refers to the solution.

The chemical potential of the solvent in the phase that contains only solvent is given by:

$$\mu^l = \mu^0 + \nabla_l p$$ \hspace{1cm} (2.38)

In osmotic equilibrium the chemical potential of the solvent in the solution is equal to that of the solvent. Thus, introducing Equations (2.38) and (2.39) into Equation (2.37) leads to:

$$\nabla_l p_s + RT \ln a_l = \nabla_l p$$ \hspace{1cm} (2.39)

Rearranging Equation (2.39) leads to:

$$\nabla_l \left( p - p_s \right) = RT \ln a_l$$ \hspace{1cm} (2.40)

The activity of the solvent in the solution $a_l^s$ is proportional to its mole fraction in the solution, $X_l^s$. Thus is:

$$\ln a_l^s = g \ln X_l^s$$ \hspace{1cm} (2.41)

Here $g$ is a proportionality factor which is referred to as osmotic coefficient.

In dilute solutions the mole fraction of the solvent is much larger than that of the solute i.e. $X_l^s >> X_s^s$. Under these conditions it can be assumed that:

$$g \ln X_l^s = g \ln (1 - X_s^s) \approx - g X_s^s$$ \hspace{1cm} (2.42)

Here $X_s^s$ is the mole fraction of the solute in the solution.
Introducing Equation (2.42) into Equation (2.40) gives the osmotic pressure of the solution as the function of the mole fraction of the solute:

$$\pi = (p^l - p^s) = - g \frac{RT}{V_l} X_{ss}^s$$ (2.43)

For dilute solutions it can be assumed that to a first approximation:

$$X_{ss}^s \approx \frac{n_{ss}^s}{n_{ls}^s}$$ (2.44)

and

$$n_{ls}^s \bar{V}_l \approx V. \quad (2.45)$$

Further is:

$$\frac{n_s^s}{V} = C_s^s$$ (2.46)

Here $n_{ss}^s$ and $n_{ls}^s$ are the number of moles of the solute and the solvent, respectively, in the solution, $V$ is the volume of the solution, $\bar{V}_l$ is the partial molar volume of the solvent and $C_s^s$ the solute concentration in the solution.

Combination of Equations (2.43) to (2.46) describes the osmotic pressure as a function of the concentration of the solute in the solution:

$$\pi = - g RT C_s^s$$ (2.47)

If the solute is a salt, as is the case in many practically relevant applications, the concentration of the individual ions must be considered when determining the osmotic pressure, i.e. the dissociation of the salt must be taken into account.

In an aqueous solution the salt is dissociated in $v_c$ cations and $v_a$ anions as indicated in Equation (2.35) and the total concentration of dissolved components is:
\[ C_c^s + C_a^s = \nu_c C_s^s + \nu_a C_{s}^s = (\nu_c + \nu_a) C_s^s \] (2.48)

Here \( C_s^s \), \( C_c^s \) and \( C_a^s \) are the concentrations of the salt, the cations and the anions in the solution and \( \nu_c \) and \( \nu_a \) are stoichiometric coefficients which determine into how many cations and anions a salt will dissociate in the solution.

Introducing Equation (2.48) into Equation (2.47) gives the osmotic pressure of an aqueous salt solution as a function of the salt concentration:

\[ \pi = - g \, RT \, (\nu_c + \nu_a) C_s^s \] (2.49)

2.4.2.2 The Donnan equilibrium and Donnan potential

In discussing the osmotic pressure it was assumed that a membrane separates a solution from a pure solvent and that the membrane is permeable only for the solvent. In this case the osmotic pressure is determined by the difference in the chemical potential of the solvent in the solution. If the solution contains charged components, i.e. ions, and the membrane is permeable for at least one ionic component, the two systems separated by the membrane will be in equilibrium if the electrochemical potential of all ions in both phases are equal. Thus, for each ion in equilibrium is:

\[ \eta_i' = \eta_i'' = \mu_i' + z_i F \phi' = \mu_i'' + z_i F \phi'' \quad (i = \text{anion or cation}) \] (2.50)

Here \( \mu \), \( \eta \) and \( \phi \) are the chemical, the electrochemical and the electrical potential, respectively, and \( F \) is the Faraday constant. The subscript \( i \) refers to anion or cation, and the superscripts (') and (") refer to two phases in equilibrium.

Electrochemical equilibrium as described by Equation (2.50) is referred to as Donnan-equilibrium. Introducing the chemical potential \( \mu_i \) as a function of pressure and composition into Equation (2.50) and rearrangement leads to the so-called Donnan potential, \( E_{\text{Don}} \) as function of the activity of the individual components and the pressure in the two phases separated by semipermeable membrane:
Equation (2.41) describes the electrical potential that will be established between two electrolyte solutions of different concentrations separated by an ion-exchange membrane. This potential difference is also referred to as concentration potential. Measurement of the concentration potential can be used to determine the permselectivity of ion-exchange membranes as will be shown later.

The Donnan potential is established not only between solutions separated by a permselective membrane but also between two phases such as a solution and an ion-exchange membrane if the ion distribution in the two phases is different. The Donnan potential between an ion-exchange membrane and an adjacent electrolyte solution is given by:

$$E_{\text{Don}} = \phi' - \phi'' = \frac{1}{z_i F} \left[ RT \ln \frac{a_i'}{a_i''} - V_i(p' - p'') \right]$$

Equation (2.51)

Here the superscripts m and s refer to the membrane and the electrolyte solution.

The Donnan potential between an electrolyte solution and an ion-exchange membrane can not be measured directly. It can, however, be calculated from the activities of the mobile ions and the pressure difference between the membrane phase and the adjacent solution, \(p_m - p_s\), which is referred to as swelling pressure (F. Helfferich 1962). The swelling pressure can be calculated as the osmotic pressure difference between the solution and the membrane phase from the chemical potential of the water in the solution and the membrane

$$p_m - p_s = -\frac{RT}{v_w} \ln \frac{a^n_w}{a^n_m}$$

Equation (2.53)

Introducing Equation (2.53) into Equation (2.40) gives the Donnan potential as a function of the ion and the water activities:

$$E_{\text{Don}} = \phi^m - \phi^s = \frac{1}{z_i F} \left[ RT \ln \frac{a_i^m}{a_i^s} - V_i(p^m - p^s) \right]$$

Equation (2.52)


\[ E_{\text{Don}} = \phi^m - \phi^s = \frac{1}{z_i F} \left[ RT \ln \frac{a_i^m}{a_i^s} + \nabla_i \left( \frac{RT}{V_w} \ln \frac{a_w^m}{a_w^s} \right) \right] \]  

(2.54)

The numerical value of \( \Delta \phi_{\text{Don}} \) is negative for the cation-exchange membrane and positive for the anion-exchange membrane in equilibrium with a dilute electrolyte solution. It can be calculated either from the cation or anion activities. Thus is:

\[ E_{\text{Don}} = \phi^m - \phi^s = \frac{1}{z_c F} \left[ RT \ln \frac{a_c^m}{a_c^s} + \nabla_c \left( \frac{RT}{V_w} \ln \frac{a_w^m}{a_w^s} \right) \right] \]  

(2.55a)

or

\[ E_{\text{Don}} = \phi^m - \phi^s = \frac{1}{z_a F} \left[ RT \ln \frac{a_a^m}{a_a^s} + \nabla_a \left( \frac{RT}{V_w} \ln \frac{a_w^m}{a_w^s} \right) \right] \]  

(2.55b)

Combination of Equations (2.55a) and (2.55b) leads to a general relation for the cation and anion distribution at the interface between a solution and an ion-exchange membrane.

\[ \frac{1}{z_c F} \left[ RT \ln \frac{a_c^m}{a_c^s} + \nabla_c \left( \frac{RT}{V_w} \ln \frac{a_w^m}{a_w^s} \right) \right] = \frac{1}{z_a F} \left[ RT \ln \frac{a_a^m}{a_a^s} + \nabla_a \left( \frac{RT}{V_w} \ln \frac{a_w^m}{a_w^s} \right) \right] \]  

(2.56)

Here \( z \) is the valence, \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the absolute temperature, \( \nabla \) is the partial molar volume, and \( a \) is the activity; the subscripts \( a, c \) and \( w \) refer to anion, cation and water, respectively and the superscripts \( s \) and \( m \) refer to the solution and the membrane, respectively.

To determine the sorption equilibrium between a strong electrolyte and an ion-exchange membrane by Equation (2.56) it can be assumed that the electrolyte is completely dissociated. Thus, one mole of electrolyte gives \( \nu_a \) moles of anions and \( \nu_c \) moles of cations and the partial molar volume of the electrolyte is the sum of the partial molar volumes of the ions. Hence is:

\[ z_a \nu_a = -z_c \nu_c \quad \text{and:} \quad \nabla_s = \nu_a \nabla_a + \nu_c \nabla_c \]  

(2.57)
Here \( \nu \) is the stoichiometric coefficient of the electrolyte, \( \bar{V} \) the partial molar volume and the subscript \( s, a \) and \( c \) refer to the salt, anion and cation, respectively. Combination of Equations (2.56) and (2.57) leads to:

\[
\left( \frac{a^s_a}{a^m_a} \right)^\nu_a \left( \frac{a^s_c}{a^m_c} \right)^\nu_c = \left( \frac{a^m_w}{a^s_w} \right) \frac{\bar{V}_s}{\bar{V}_w}
\]  

Equation (2.58) is the general thermodynamic form of the Donnan equilibrium for the sorption of an electrolyte from an adjacent solution.

2.4.2.3 The Donnan exclusion and membrane permselectivity

The Donnan equilibrium describes the relation between the concentrations of the different ionic species in the membrane and the adjacent electrolyte solution. The ion concentration in the membrane and especially that of the co-ion which is the ion carrying the same charge as the membrane matrix is of prime importance for the membrane permselectivity. To obtain a completely permselective membrane the co-ion should completely be excluded from the membrane phase. This exclusion is generally referred to as Donnan exclusion. The concentration of the co-ions in the membrane can be derived from Equation (2.58) by the application of electroneutrality condition and by substituting the ion activities by the ion concentrations and the corresponding activity coefficients.

The ion activity is given by:

\[
a^m_a = C^m_a \gamma_a^m; a^s_a = C^s_a \gamma_a^s; a^m_c = C^m_c \gamma_c^m \text{ and } a^s_c = C^s_c \gamma_c^s
\]

(2.59)

The electroneutrality conditions in the membrane and solution lead to:

\[
|z_{cou}| C^m_{cou} = C^m_f + |z_{co}| C^m_{co} \text{ and } |z_{cou}| C^s_{cou} = |z_{co}| C^s_{co}
\]

(2.60)
Here $C_{\text{f}}^m$ is the concentration of fixed ion groups of the ion-exchange membrane and $C_{\text{cou}}$ and $C_{\text{co}}$ are the counter- and the co-ions, i.e. the ions which carry the opposite and the same charge as the membrane, respectively; the superscripts $m$ and $s$ refer to the membrane and the adjacent solution.

Introducing Equations (2.59) and (2.60) into Equation (2.2.57) leads to:

$$
\left(\frac{C_{\text{cou}}^m}{C_{\text{co}}^s}\right)^{v_{\text{co}}} = \left(\frac{|z_{\text{co}}| C_{\text{co}}^s}{|z_{\text{co}}| C_{\text{co}}^m + C_{\text{f}}^m}\right)^{v_{\text{co}}} \gamma_{\pm}^s \gamma_{\pm}^m \frac{\gamma_{aw}^m}{\gamma_{aw}^s} \frac{\bar{V}_s}{\bar{V}_w}
$$

(2.61)

Here $C$ is the concentration of ion species, $z$ the electrochemical valence, $v$ the number of ions in a mole, $\bar{V}$ the partial molar volume, and $\gamma$ the activity coefficient. The subscripts co, f, w, s, and $\pm$ refer to the co-ion, the fixed ion of the membrane, the water, the salt, and a mean value of the positively and negatively charged ions of an electrolyte, respectively. The superscripts $m$ and $s$ refer to the membrane and the adjacent solution.

Equation (2.61) describes the distribution of the co-ions between an ion-exchange membrane and the adjacent solution. It can be shown that for most practical applications the swelling pressure term in Equation (2.61) can be neglected (Helfferich 1962), and thus:

$$
\left(\frac{a_{aw}^m}{a_{aw}^s}\right) \frac{\bar{V}_s}{\bar{V}_w} \approx 1
$$

(2.62)

If it is further assumed that for very dilute solutions the co-ion concentration in the membrane is small compared to the fixed ion-concentration, i.e. $C_{\text{co}}^m \ll C_{\text{f}}^m$ and the electrolyte is monovalent, Equation (2.61) can be solved to give a very simple relation for the co-ion concentration in the membrane:

$$
C_{\text{co}}^m = \frac{C_{\text{co}}^s}{C_{\text{f}}^m} \left(\frac{\gamma_{\pm}^s}{\gamma_{\pm}^m}\right)^2
$$

(2.63)
Here \( C_{co}^m \) and \( C_{co}^s \) are the co-ion concentrations in the membrane and in the electrolyte solution, respectively; \( C_f^m \) is the concentration of the fixed ions in the membrane, and \( \gamma_\pm^s \) and \( \gamma_\pm^m \) are the average activity coefficients of the salt in the electrolyte solution and the membrane, respectively.

Equation (2.63) describes the Donnan exclusion only to a first approximation. Considerable deviation of measured co-ion concentrations in the membrane from those calculated by Equation (2.63) is often obtained. The differences between the observed and the calculated membrane behaviour are mainly due to the non-uniformities in the distribution of the fixed ions in the membrane, which results from structural irregularities on a molecular level and from the influence of the electric field on the ion distribution.

In general, however, the Donnan exclusion equilibrium and thus the selectivity of an ion-exchange membrane depend on: (1) The concentration of the fixed ions, (2) the valence of the co-ions, and (3) the concentration of the electrolyte solution, and (4) the affinity of the ion-exchange material with respect to the counter-ions. The permselectivity of an ion-exchange membrane increases with increasing concentration of the fixed ions with decreasing electrolyte solution concentration and with decreasing chemical valence of the co-ions.

2.4.3 Mathematical description of mass transport in membranes
As indicated earlier mass transport between two homogeneous systems through a membrane may be the result of diffusion, convection or migration depending on the driving forces and the structure of the membrane.

A mass transport process is referred to as diffusion when individual components permeate a matrix independent of each other by random movement under the driving force of a chemical potential gradient. The permeation rate in a diffusion process depends on the magnitude of the driving force, i.e. the chemical potential gradient of the diffusing component and on its diffusion coefficient which is determined by friction between the diffusing component and other components in a mixture.
A mass transport process is referred to as \textit{convection} when bulk flow occurs under the driving force of a hydrostatic pressure difference relative to a matrix which acts as a frame of reference. The flow velocity depends on the hydrostatic pressure difference and hydrodynamic permeability of the matrix which is determined by the friction between the solution and the matrix.

A mass transport is referred to as \textit{migration} when charged components move through a matrix under the driving force of an electrical potential difference. The migration rate depends on the electrical potential gradient and the mobility of the components in the matrix. The mobility of a component is directly related to its diffusion coefficient and is determined by the friction between the migrating component and other components in a mixture.

In membrane processes all three forms of mass transport can contribute to the overall flux. Generally, however, one transport form is dominant while the others contribute to a lesser extent to the overall mass flux. In micro- and ultrafiltration convection of a bulk solution is the dominant form of transport while diffusion is generally insignificant. In reverse osmosis matter is transported through the membrane mainly by diffusion of individual molecules through a more or less homogeneous membrane matrix, but convection can become significant with high flux membranes. In electrodialysis migration of ions in an electric field is the dominant form of transport, but under certain process conditions diffusion and convection can also become relevant.

The mass transport through membranes can be described by various mathematical relations. Most of them are semi-empirical, postulating membrane models, such as Fick's law, Hagen-Poiseuille's law and Ohm's law. A more comprehensive description, which is independent of the membrane structure and thus any membrane model is based on a general phenomenological equation which connects the fluxes of electrical charges and individual components with the driving forces by a linear relation (Onsager 1931):

\[ J_i = \sum_k L_{ik}X_k \]  \hspace{1cm} (2.64)

Here \( J \) is a flux per unit area and generalized \( X \) is a driving force, the subscripts \( i \) and \( k \) refer to individual components and electrical charges, \( L \) is a phenomenological coefficient relating the fluxes to the driving forces.
For multi-component systems with fluxes of individual components and electrical charges, Equation (2.64) can be written as a matrix in which the diagonal coefficients relate the fluxes to the directly corresponding driving forces, and the cross-coefficients express the coupling of fluxes with non-conjugated driving forces.

\[
\begin{align*}
J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n \\
J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n \\
&\vdots \\
J_n &= L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n 
\end{align*}
\] (2.65)

Thus, Equation (2.64) describes the mass transport through a membrane not only as a linear function of the corresponding driving forces as, e.g. Fick's or Ohm's law, but it considers also a possible kinetic coupling between different fluxes.

In membrane processes generally large fluxes are desirable which are the result of spontaneous, i.e. irreversible processes with a positive entropy production. The relation between the entropy production and the mass transport is given in Equations (2.31) and (2.34). Applying this relation to the phenomenological Equation (2.64) leads to:

\[
T \frac{dS}{dt} = \Psi = \sum_{i} J_i X_i = \sum_{i} \sum_{k} L_{ik} X_k X_i > 0 
\] (2.66)

Here \(\Psi\) is the dissipation function, \(X\) is a driving force, the subscripts \(i\) and \(k\) refer to individual components, momentum, and electrical charges, \(L\) is a phenomenological coefficient relating the fluxes to the driving forces.

By introducing Equation (66) into (64) it can be shown (Katchalsky and Curran 1967) that the diagonal coefficients are always positive, while the cross-coefficients may be positive or negative. For a two-component system which has 2 driving forces and 4 phenomenological coefficients the dissipation function is given by:

\[
\psi = (L_{11}X_1 + L_{12}X_2)X_1 + (L_{21}X_1 + L_{22}X_2)X_2 \geq 0 
\] (2.67)
or rearranging by:

\[ \psi = L_{11}X_1^2 + (L_{21}X_1 + L_{21}X_2)X_1X_2 + L_{22}X_2^2 \geq 0 \quad (2.68) \]

Since the entropy production for all positive and negative values of \( X_1 \) and \( X_2 \) must be positive the phenomenological coefficients must satisfy the following relation:

\[ L_{11}L_{22} - L_{12}L_{21} \geq 0 \quad (2.69) \]

and

\[ L_{11} \geq 0 \quad \text{and} \quad L_{22} \geq 0 \quad (2.70) \]

Thus, the cross coefficient may be positive or negative to satisfy Equation (2.69). Their number, however, is reduced by the Onsager relation, which is:

\[ L_{ik} = L_{ki} \quad (2.71) \]

Another approach to describe the mass transport in membrane processes is based on a relation developed by Maxwell and Stefan around 1870 and which was extended by Spiegler (Spiegler 1958). In this relation the forces are expressed as a linear function of the fluxes:

\[ X_i = \sum_k R_{ik}J_k \quad (2.72) \]

Here \( R \) is a phenomenological coefficient relating driving forces and fluxes.

The coefficient \( L \) of Equation (2.64) has the dimension of a generalized conductance and is expressed by a flux per unit force and the coefficient \( R \) in Equation (2.72) has the dimension of a generalized resistance and is expressed by a unit force divided by a flux. Thus is:

\[ L_{ik} = \left( \frac{J_i}{X_k} \right)_{X_i} \quad \text{and} \quad R_{ik} = \left( \frac{X_i}{J_k} \right)_{J_i} \quad (73) \]
The Maxwell-Stefan approach is based on the assumption that in a steady state flux the driving forces acting on a component \( i \) are equal to the sum of the friction forces between \( i \) and other components in the system.

The flux of a component in a mixture is always expressed relative to another component which is used as a frame of reference. Thus, the flux \( J_i \) of a component \( i \) in a mixture relative to a component \( k \) is:

\[
J_i = C_i (v_i - v_k)
\]  

(2.74)

Here \( v \) is the linear velocity of the component and \( C \) the concentration.

The flux of an individual component is always proportional to its linear velocity relative to the velocity of another component which is used as a frame of reference. Thus, the number of independent fluxes in a given system is equal to the total number of components in the system minus the one used as reference. A system containing a membrane with \( n \) components -including the membrane- has \( n - 1 \) independent fluxes. In membrane processes generally the fluxes through the membrane are of interest. Therefore, the membrane is used as frame of reference and its velocity is assumed zero.

If viscous flow is excluded the Maxwell-Stefan equation is given by:

\[
X_i = \sum_k C_i f_{ik} (v_i - v_k) = \sum_k C_i \frac{RT}{\mathcal{D}_{ik}} (v_i - v_k)
\]  

(2.75)

Here \( X \) is the driving force, \( C \) is the concentration, \( v \) is the linear velocity, \( f \) is the friction coefficient, and \( \mathcal{D} \) is the Maxwell-Stefan diffusion coefficient. The subscripts \( i \) and \( k \) refer to individual components.

Combination of Equations (2.64), (2.72) and (2.75) provides the relation between the various terms of the phenomenological equations and the Maxwell-Stefan equations.

\[
\sum_i L_{ik} = \frac{1}{\sum_i R_{ik}} = \frac{1}{\sum_i f_{ik}} = \sum C_i \frac{\mathcal{D}_{ik}}{RT}
\]  

(2.76)

64
Equations (2.72) and (2.75) provide the same complete description of transport processes through a membrane separating two homogeneous mixtures as does the phenomenological Equation (2.64). The only other boundary condition relevant for a system which contains charge components is that electroneutrality has to be fulfilled at all times on a macroscopic scale. All phenomena observed in membrane systems, such as osmosis, electroosmosis, and the diffusion of individual components, a viscous flow of a bulk solution, an electric current, or the build up of an osmotic pressure, a streaming and a diffusion potential as well as the different technically relevant membrane processes can be described by applying the Equations (2.64) or (2.72). The practical value of the equations, however, is rather limited. First of all, they are only applicable close to equilibrium because of the assumed linear relationships between fluxes and driving forces. Furthermore, the many different coefficients are difficult to determine by independent measurements. The treatment becomes even more complicated if the membrane consists of a heterogeneous medium such as a micro- and ultrafiltration membrane where viscous flow is the dominant means of mass transfer in the pores when a hydrostatic pressure is applied as a driving force but diffusion and migration can exist both in the pore medium and the solid membrane matrix. However, under certain approximations and by neglecting coupling of fluxes Equations (2.64) and (2.72) can be reduced to give very simple relations, such as Ohm's or Fick's law, and the phenomenological coefficients can be expressed by the electrical resistance or the diffusion coefficient.

Through the coupling of fluxes it becomes obvious that a transport of components may be obtained without a directly related driving force. The magnitude of the fluxes obtained through a coupling with other fluxes depends on the coupling coefficient. In many cases the coupling between fluxes can be neglected. In some cases, however, it can be significant. For instance, the coupling of water with an ion flux can lead to a significant water transport through a membrane.

Mass transport in membrane processes can be achieved by applying different driving forces, such as pressure, concentration or electrical potential gradients to a feed mixture as discussed in detail earlier. The different driving forces result in different membrane processes in which also different membrane structures are utilized. In micro- and ultrafiltration, for example, porous membranes are applied that separate the various components of a mixture according to their size. The transport is mainly based on convection and the driving force is a hydrostatic pressure
gradient. In reverse osmosis, gas separation and pervaporation dense films are used as selective barrier for the transport of low molecular weight components. The driving force is a hydrostatic or partial pressure difference between a feed mixture and a permeate. The transport is based on diffusion. In dialysis a concentration difference is used to achieve the desired mass transport which is also based on diffusion. In electrodialysis an electrical potential gradient across a membrane leads to a migration of charged components.

The mass transport in the various membrane processes can be described by the phenomenological equations which can be simplified by certain approximations that are based on postulating certain membrane models such as the solution-diffusion model, the porous membrane model and the ion-exchange membrane model.

2.4.3.1 Mass transport in dialysis
Dialysis is carried out under isobaric conditions, and there is no temperature or electrical potential gradient. The principle of the process is depicted in Figure 6 which shows a liquid solution containing a solvent and molecular components of different molecular weight or size, referred to as feed solution separated by a membrane from the solvent referred to as dialysate. Due to the driving force of a concentration difference the components will diffuse through the membrane. Their fluxes through the membrane and thus their separation is determined by their permeation velocity in the membrane matrix. There are different forms of dialysis depending on the constituents of the feed solution and the structure of the membrane. The most simple form is dialysis of neutral components in a neutral membrane, i.e. a membrane that does not carry any electrical charges.
Fig. 2.6 Schematic drawing illustrating the principle of dialysis with two neutral components of different size

*Dialysis of neutral components through a membrane that carries no electrical charges*

The mass flux in dialysis of a mixture which contains neutral components only through a membrane does not carry any positive or negative charges can be expressed by the phenomenological equation or the Maxwell-Stefan relation which can then be related to Fick's law by certain approximations.

Assuming the most simple case, i.e. a membrane and two uncharged components, e.g. a solvent and a solute. For this system two independent fluxes are obtained if the membrane is used as frame of reference. The fluxes of the two components are given according to Equations (2.65) and (2.75) by:

\[
J_1 = -L_{1m} \frac{d \mu_1}{dz} + L_{12} \frac{d \mu_2}{dz} \tag{2.77a}
\]

\[
J_2 = +L_{21} \frac{d \mu_2}{dz} - L_{2m} \frac{d \mu_2}{dz} \tag{2.77b}
\]

and
Here $\frac{d\mu_1}{dz}$ and $\frac{d\mu_2}{dz}$ are the gradients in the chemical potentials of the components 1 and 2 in direction perpendicular to the membrane surface, $C_1$ and $C_2$ are the concentrations of the components 1 and 2, $v_1$, $v_2$, and $v_m$ are the velocities of the components 1, 2 and the membrane, respectively. $\mathcal{D}_{1m}$, $\mathcal{D}_{2m}$, $\mathcal{D}_{12}$ and $\mathcal{D}_{21}$ are the Maxwell-Stefan diffusion coefficients of the components 1 and 2 in reference to the membrane and to each other. The membrane is used as frame of reference for the fluxes of the two components and thus is the velocity of the membrane $v_m = 0$.

Introducing the Equation (2.26) which relates the chemical potential of a component at constant pressure to its activity, into Equations (2.77) and (2.78) leads to:

\[
-J_1 = -L_{1m}RT \frac{d\ln a_1}{dz} - L_{12}RT \frac{d\ln a_2}{dz} \quad (2.79a)
\]

\[
-J_2 = -L_{21}RT \frac{d\ln a_1}{dz} - L_{2m}RT \frac{d\ln a_2}{dz} \quad (2.79b)
\]

and

\[
-RT \frac{d\ln a_1}{dz} = \frac{RT}{\mathcal{D}_{1m}} C_1 v_1 + \frac{RT}{\mathcal{D}_{12}} C_1 (v_1 - v_2) \quad (2.80a)
\]

\[
-RT \frac{d\ln a_2}{dz} = \frac{RT}{\mathcal{D}_{2m}} C_2 v_2 + \frac{RT}{\mathcal{D}_{21}} C_2 (v_2 - v_1) \quad (2.80b)
\]
For neutral components kinetic coupling of fluxes can generally be neglected and to a first approximation Equations (2.79) and (2.80) can be written as:

\[ J_1 = -L_1 m RT \frac{d \ln a_1}{dz} \] (2.81a)

and

\[ J_2 = -L_2 m RT \frac{d \ln a_2}{dz} \] (2.81b)

and

\[ -\frac{d \ln a_1}{dz} = \frac{v_1}{D_{1m}} \] (2.82a)

and

\[ -\frac{d \ln a_2}{dz} = \frac{v_2}{D_{2m}} \] (2.82b)

When the activities in Equations (2.81) and (2.82) are replaced by the activity coefficients \( \gamma_1 \) and \( \gamma_2 \) and the concentrations \( C_1 \) and \( C_2 \), the fluxes are given as a function of the concentration difference:

\[ J_1 = -L_1 m RT \frac{d \ln (\gamma_1 C_1)}{dz} = -L_1 m \frac{RT}{C_1} \left( 1 + \frac{d \ln \gamma_1}{d \ln C_1} \right) \frac{dC_1}{dz} \] (2.83a)

and

\[ J_2 = -L_2 m RT \frac{d \ln (\gamma_2 C_2)}{dz} = -L_2 m \frac{RT}{C_2} \left( 1 + \frac{d \ln \gamma_2}{d \ln C_2} \right) \frac{dC_2}{dz} \] (2.83b)

and

\[ C_1 v_1 = J_1 = -D_{1m} \frac{d \ln \gamma_1 C_1}{dz} = -D_{1m} \left( 1 + \frac{d \ln \gamma_1}{d \ln C_1} \right) \frac{dC_1}{dz} \] (2.84a)

and
\[ C_2 \gamma_2 = J_2 = -\mathcal{D}_2m \frac{d \ln \gamma_2 C_2}{dz} = -\mathcal{D}_2m \left( 1 + \frac{d \ln \gamma_2}{d \ln C_2} \right) \frac{dC_2}{dz} \quad (2.84b) \]

Comparison of Equations (2.83) and (2.84) with Fick's law of diffusion which is given by:

\[ J_i = -D_i \frac{dC_i}{dz} \quad (i = 1, 2) \quad (2.85) \]

gives a relation between the Fick's diffusion coefficient and the phenomenological coefficients

\[ D_i = L_{im} \frac{RT}{C_i} \left( 1 + \frac{d \ln \gamma_i}{d \ln C_i} \right) \quad (i = 1, 2) \quad (2.86) \]

and between the Maxwell-Stefan and Fick's diffusion coefficient

\[ D_i = \mathcal{D}_{im} \left( 1 + \frac{d \ln \gamma_i}{d \ln C_i} \right) \quad (i = 1, 2) \quad (2.87) \]

Equations (2.85), (2.86) and (2.87) indicate that the mass transport in dialysis with feed solutions containing neutral components can be described adequately by Fick's law only if there is no coupling of fluxes and if the activity coefficient of the components in the membrane is unity, i.e. if their activities are identical to their concentrations. This is, however, the case in most practical applications.

*Dialysis of solutions containing charged components in a neutral membrane*

If feed solutions with charged components such as salts, acids or bases are treated by dialysis there is an additional boundary condition which must be satisfied on a macroscopic scale at any time and that is the electroneutrality requirement. For a system consisting of a membrane and solutions with various ions the electroneutrality condition requires:

\[ \sum_{a} z_a C_a = \sum_{c} z_c C_c \quad (2.88) \]
Here \( z \) is the valance and \( C \) the concentration, the subscripts \( a \) and \( c \) refer to anion and cation, respectively.

If the membrane contains fixed electrical charges they must be included in Equation (2.88) which then is:

\[
\sum z_i C_i = z_i^m C_i^m \quad (i = \text{anion, cation}) \tag{2.89}
\]

Here the superscript \( m \) refers to ions that are fixed to the membrane matrix. For a cation-exchange membrane \( z_i^m \) is -1 and for an anion-exchange membrane \( z_i^m \) is +1. For a membrane that does not carry electrical charges \( z_i^m \) is 0.

If there is no electrical current the conservation of the electrical charge requires that cations and anions will move in the same direction. Thus is:

\[
\sum z_a J_a = \sum z_c J_c \tag{2.90}
\]

Here \( J \) is the flux and the subscripts \( a \) and \( c \) refer to anions and cations, respectively.

The concentration of the electrolyte, e.g. a salt is related to that of the individual ions by:

\[
C_a = \alpha \nu_a C_s \text{ and } C_c = \alpha \nu_c C_s \tag{2.91}
\]

Here \( \alpha \) is the dissociation constant of the electrolyte, \( \nu \) is a stoichoimetric coefficient and the subscript \( s \) refers to the undissociated electrolyte.

For a completely dissociated monovalent salt such as NaCl \( \alpha \) and \( \nu \) are 1. For a salt such as CaCl\(_2\) \( \nu_c \) is 1 and \( \nu_a \) is 2.

By describing the flux of an electrolyte through a membrane the ions can be treated as individual components and if a kinetic coupling is neglected the fluxes of the ions can be described by Equations (2.83) and (2.84). Although there is no kinetic coupling between different ions there is always the electroneutrality requirement expressed in Equations (2.88) and (2.89). The consequence of the electroneutrality requirement is that in diffusion of an electrolyte which
consists of a cation and an anion with significantly different diffusivities in the membrane such as HCl the faster moving ion, in this case the hydrogen ion, will cause a minute charge imbalance and thus an electrical potential gradient. This potential gradient is referred to as diffusion potential and although it might be very small it will slow the hydrogen ion down and speed up the chloride ion so that both will move together with the same velocity.

The fluxes of cations, anions and the electrolyte of a monovalent electrolyte in a membrane that does not carry electrical charges are obtained applying Equation (2.83):

\[
J_c = -L_{cm} \frac{RT}{C_c} \left( 1 + \frac{d \ln \gamma_c}{d \ln C_c} \right) \frac{dC_c}{dz}, \quad (2.92)
\]

\[
J_a = -L_{am} \frac{RT}{C_a} \left( 1 + \frac{d \ln \gamma_a}{d \ln C_a} \right) \frac{dC_a}{dz} \quad (2.93)
\]

and

\[
J_s = -L_{sm} \frac{RT}{C_s} \left( 1 + \frac{d \ln \gamma_s}{d \ln C_s} \right) \frac{dC_s}{dz} \quad (2.94)
\]

Because of the charge conservation requirement expressed in Equation (2.88) it is:

\[
J_s = J_c = J_a \quad (2.95)
\]

The chemical potential of a monovalent salt is given by the sum of the chemical potential of the cation and the anion.

\[
\mu_s = \mu_c + \mu_a \quad (2.96)
\]

Combination of Equations (2.88) to (2.96) and assuming that the activity coefficients of the individual ions in the mixture are identical to the activity coefficient of the electrolyte and that the membrane does not carry fixed charges leads to:
\[
L_{sm} = 2 \left( \frac{1}{L_{cm}} + \frac{1}{L_{am}} \right)^{-1} \tag{2.97}
\]

Analogous can the diffusivity of the electrolyte be expressed by the diffusivities of the individual ions:

\[
D_{sm} = 2 \left( \frac{1}{D_{cm}} + \frac{1}{D_{am}} \right)^{-1} \tag{2.98}
\]

Introduction of Equation (2.97) into Equation (2.94) leads to:

\[
J_s = -2 \left( \frac{L_{cm}L_{am}}{L_{cm} + L_{am}} \right) \frac{RT}{C_s} \left( 1 + \frac{d \ln \gamma_s}{d \ln C_s} \right) \frac{dC_s}{dz} \tag{2.99}
\]

Analogous the salt flux can be expressed by the Stefan-Maxwell diffusion coefficients:

\[
J_s = -2 \left( \frac{D_{cm}D_{am}}{D_{cm} + D_{am}} \right) \left( 1 + \frac{d \ln \gamma_s}{d \ln C_s} \right) \frac{dC_s}{dz} \tag{2.100}
\]

when the phenomenological coefficients are replaced by the Maxwell-Stefan diffusion coefficients.

2.4.3.2 Diffusion of a multi ion electrolyte in neutral and an ion-exchange membrane

Equations (2.99) and (2.100) respectively describe the transport of a single electrolyte under the driving force of a concentration or activity gradient through a neutral membrane. The situation, however, becomes more complex if a mixture contains more than one electrolyte and if the membrane carries fixed charges. In this case certain ions might be transported against their concentration gradient as shown in the following example.

In Figures 7 a), b) and c) the flux of ions through an interphase such as a membrane as a result of a concentration difference is shown schematically. In Figure 7a) a neutral membrane separates a solution with a single electrolyte, which in this case is assumed to be HCl. Due to the
electroneutrality requirements the concentrations and fluxes of the $\text{H}^+$- and the $\text{Cl}^-$-ions are equal at any point in the system. Due to the higher mobility of the $\text{H}^+$-ions an electrical potential is established that slows down the $\text{H}^+$-ions and accelerates the $\text{Cl}^-$-ions.

Figure 7b) shows a system where the solution separated by the membrane contains a small amount of NaCl in addition to the HCl. The fluxes of all ions in the system are determined by their concentration gradients in the membrane and an electrical potential gradient which is established by the differences between the diffusivities of the $\text{H}^+$-ions and the $\text{Cl}^-$-ions. This electrical potential gradient is increasing the flux of the chloride ions and decreasing the flux of the $\text{H}^+$- and the $\text{Na}^+$-ions and eventually reversing the flux of the $\text{Na}^+$-ions if the concentration gradient driving force for the $\text{Na}^+$-ions is exceeded by the electrical potential driving force as indicated in Figure 7b).

If the two solutions, as indicated in Figure 7c), are separated by a negatively charged cation-exchange membrane which will exclude the negatively charged Cl-ions more or less completely there will hardly be any flux of Cl-ions and the charges carried by the $\text{H}^+$-ions in one direction must be compensated by the charges carried by the $\text{Na}^+$-ions in the opposite direction. Thus, the flux of $\text{H}^+$-ions due to a concentration gradient driving force induces a flux of $\text{Na}^+$-ions against their concentration gradient. The transport described in Figure 7c) is the basis for a membrane process which is referred to as Donnan dialysis.
In Donnan dialysis with a strictly permselective ion-exchange membrane the fluxes of the co-
ions are 0 and the sum of the fluxes of the counter-ions is also 0. Thus, there is no net transport
of electrical charges across the membrane, i.e. there is no electrical current and the conservation
of charges requires:

$$\sum z_i J_i = 0$$  \hspace{1cm} (2.101)

Here J is the flux of ions through the membrane and the subscript i refers to counter-ions.
Although the sum of the counter-ions is 0 the magnitude of the individual ion fluxes depends on
the difference in their activities in the two phases separated by the membrane.

For a system that consists of two solutions of different concentrations of two monovalent
electrolytes separated by a strictly permselective membrane as illustrated in Figure 2.7c) the

Fig. 2.7 Schematic drawing illustrating the fluxes across membranes which separate electrolyte
solutions of different concentrations: a) shows one electrolyte (HCl), b) two electrolytes (HCl
and NaCl) separated by a neutral membrane and c) shows two electrolytes (HCl and NaCl)
separated by a negatively charged cation-exchange membrane
transport of a counter-ion, e.g. a Na\(^+\)-ion is the result of a flux of another counter-ion, e.g. H\(^+\)-ion in opposite direction. Since the mobility of the H\(^+\)-ion in the membrane is higher than that of the Na\(^+\)-ion a small electrical potential will be created which slows down the H\(^+\)-ion flux and accelerates the Na\(^+\)-ion flux in the opposite direction. The flux of the H\(^+\)-ions, which is identical to that of the Na\(^+\)-ions, is given by:

\[
J_{H^+} = -2 \left( \frac{L_{H^+ m} L_{Na^+ m}}{L_{H^+ m} + L_{Na^+ m}} \right) RT \frac{d \ln a_{H^+}}{dz} = J_{Na^+}
\] (2.102)

The transport of Na\(^+\)-ions due to the H\(^+\)-ion flux results in a build-up of an activity gradient of the Na\(^+\)-ions which is causing a back transport. When the Na\(^+\)-ion flux caused by the activity gradient is identical to that caused by H\(^+\)-ion flux equilibrium is reached and there will be no further ion transport through the membrane. This equilibrium, which is referred to as Donnan equilibrium, is given by:

\[
d \ln a_{H^+} = d \ln a_{Na^+}
\] (2.103)

The Donnan equilibrium between two solutions with different Na\(^+\)-ion and H\(^+\)-ion concentrations separated by a permselective cation-exchange membrane is:

\[
\frac{a'_{Na^+}}{a_{Na^+}} = \frac{a'_{H^+}}{a_{H^+}}
\] (2.104)

The superscripts ' and " refer to the two solutions separated by the membrane.
Donnan dialysis plays an important role in water softening and Equation (2.104) determines which minimum and maximum concentrations of a counter-ion can be achieved by a given flux of another counter ion.
2.4.3.3 Membrane mass transport in electrodialysis

In electrodialysis the mass transport is the result of an electrochemical potential gradient across the membrane, i.e. a gradient in the chemical and electrical potential. An electrical potential driving force is acting on charged components only and in such a way that negatively charged components, i.e. the so-called anions migrate in the direction towards the positively charge anode and the positively charged cations migrate towards the negatively charge cathode, i.e. cations and anions move in different directions and have to be considered separately. The principle of the electrodialysis is illustrated in Figure 2.8. In electrodialysis cation-exchange membranes carrying fixed negative electric charges and anion-exchange membranes carrying positive fixed charges are placed in alternating series between two electrodes. Cation and anion-exchange membranes form individual cells filled with an electrolyte containing feed solution. If an electric potential between the electrodes is established the cations migrate towards the negatively charged cathode while the anions migrate towards the positively charged anode. Cations can easily permeate a cation-exchange membrane but will be retained by an anion-exchange membrane. Vice versa, anions permeate the anion-exchange membrane but will be retained by the cation-exchange membrane. Thus, ions will be accumulated in alternating cells forming the concentrate solution while the other cells get depleted and form the diluate solution.
The mass transport in electrodialysis under isobaric conditions utilizing an electrical potential difference as driving force can be described either by the phenomenological Equations (2.64) and (2.72) or by the Nernst-Planck equation which can be derived under certain assumptions from the phenomenological equations. The phenomenological coefficients and the Maxwell-Stefan diffusion coefficient can then be related to constants such as electric resistance and ion mobility or ion diffusivity.

In electrodialysis the flux of a single ion is given by:

$$J_i = \sum L_{ik} \frac{dn_k}{dz} = \sum L_{ik} \left( z_i F \frac{d\phi}{dz} + RT \frac{d \ln a_i}{dz} \right)$$

(2.105)

Assuming an ideal solution, i.e. the activity of a component is identical to its concentration and no kinetic coupling between individual components, and expressing the phenomenological

---

Fig. 2.8  Schematic drawing illustrating the principle of an electrodialysis process
The Fick's diffusion coefficient Equation (2.105) becomes identical with the Nernst-Planck flux equation which is given by:

\[ J_i = D_i \frac{dC_i}{dz} + D_i \frac{z_i C_i F}{RT} \frac{d\phi}{dz} \]  

(2.106)

Here \( D_i \) is the diffusion coefficient of the component \( i \) in reference with the membrane and the first term \( D_i \frac{dC_i}{dz} \) represents the diffusion, the second term \( D_i \frac{z_i C_i F}{RT} \frac{d\phi}{dz} \) the migration.

Thus, the Nernst-Planck equation is an approximation of the more general phenomenological equation, which will be used in the further discussion.

The current in electrodialysis is related to the flux of ions by:

\[ i = F \sum_i z_i J_i \]  

(2.107)

and to the electrical potential driving force by introducing Equation (2.105) into (2.107):

\[ i = F^2 \sum_i z_i^2 L_{ik} \left( \frac{d\phi}{dz} + \frac{RT}{z_i F} \frac{d\ln a_i}{dz} \right) \]  

(2.108)

Here \( i \) is the current density, \( \eta \) and \( \phi \) are the electrochemical and the electrical potentials, respectively, \( a \) is the activity, \( J \) the flux, \( L \) the phenomenological coefficient, \( F \) the Faraday constant, \( z \) the valence, and \( dz \) is a directional co-ordinate perpendicular to the membrane surface; the subscripts \( i \) and \( k \) refer to ions and to all components in the system, respectively.

The term \( \frac{RT}{z_i F} \frac{d\ln a_i}{dz} \) has the dimension of an electrical potential gradient and represents the concentration potential established between electrolyte solutions of different concentrations. In electrodialysis the concentration potential counteracts the applied potential.

The electrical potential gradient in Equation (2.108) can explicitly be expressed by:
The current is related to the electrical potential gradient by Ohm’s law according to:

\[
i = \kappa \frac{d\phi}{dz}
\]  

(2.110)

Here \( \kappa \) is the specific conductivity which is given by:

\[
\kappa = \sum z_i C_i \lambda_i = F \sum z_i C_i u_i = \sum z_i C_i m_i
\]  

(2.111)

Here \( F \) is the Faraday constant and \( z_i \) the valence, \( \lambda_i \) is the equivalent conductivity, \( C_i \) the concentration, \( u_i \) the migration velocity, and \( m_i \) the mobility, respectively, of the ion \( i \).

Assuming migration only the specific conductivity of an electrolyte solution can be expressed as a function of the phenomenological coefficients \( L_{ik} \). A comparison of Equations (2.108), (2.110) and (2.111) relates the specific conductivity \( \kappa \), the ion migration velocity, and the ion mobility to the phenomenological coefficients.

\[
\kappa = F^2 \sum \frac{z_i^2}{L_{ik}} = F \sum z_i C_i u_i = \sum z_i C_i m_i
\]  

(2.112)

In electrodialytical processes the current flowing through the stack is according to Equation (107) proportional to the sum of all ion-fluxes. However, the current is not always carried equally by all ions. Especially in ion-exchange membranes the current is carried preferentially by the counter-ions. The portion of the current that is carried by one ion species is determined by the ion transport or ion transference number which is given by:

\[
T_i = \frac{z_i J_i}{\sum z_i J_i} \quad (i = \text{anion and cation})
\]  

(2.113)
Here $T_i$ is the transport number of the component $i$ indicating the fraction of the total current carried by the ion $i$, and $t_i$ is the transference number determining the number of moles of the ion $i$ transported per mole of electrons, i.e. per Faraday.

The transport number is directly related to the ion concentration and their mobility, and its sum is one. Thus is:

$$T_i = \frac{z_i C_i m_i}{\sum_i z_i C_i m_i}$$ \hspace{1cm} (2.115)

Furthermore is:

$$\sum_i T_i = 1$$ \hspace{1cm} (2.116)

and

$$\sum_i z_i t_i = 1$$ \hspace{1cm} (2.117)

The transport numbers of different salt ions in the solution are not very different. In an ion-exchange membrane, however, there are the "fixed" ions of the membrane in addition to the mobile ions of the electrolyte. The fixed ions do not contribute to the transport of electrical charges and their transport number is therefore 0. Combination of Equations (2.105) and (2.113) gives the transport number as a function of the phenomenological coefficient.

$$T_i = \frac{z_i L_{ik}}{\sum_i z_i L_{ik}}$$ \hspace{1cm} (2.118)

If a kinetic coupling of fluxes can be neglected the cross coefficient $L_{ik}$ in the flux equation disappears and the diagonal coefficient $L_{ii}$ must be considered. Introducing this approximation
and combining Equations (2.109) to (2.118) expresses the flux of an ion in electrodialysis as a function of three terms, i.e. the diffusion as a function of an activity gradient, the migration due to the concentration potential gradient, and the transference by the electrical current as indicated in the following relation:

\[
J_i = -L_{ii}RT \left( \frac{d \ln a_i}{dz} - \sum_i T_i \frac{d \ln a_i}{dz} \right) + T_i \frac{i}{z_i F}
\]  

(2.119)

The ion activities in Equation (2.119) can be expressed by the ion concentrations and the corresponding activity coefficient and the phenomenological coefficient by the Maxwell-Stefan diffusion coefficient as indicated in Equation (2.84):

\[
J_i = -D_{ii} \left( \frac{d C_i}{dz} - C_i \sum_i T_i \frac{d C_i}{dz} \right) + T_i \frac{i}{z_i F}
\]  

(2.120)

Equations (2.119) and (2.120) describe the flux of ions as a function of a concentration and an electrical potential gradient, the ion transport number and an ion mobility term expressed by the phenomenological coefficient or the diffusion coefficient. The Equation (2.120) describes the transport of the ions of a monovalent single salt in a solvent such as water or in a membrane which are used as frame of reference. Thus, in water the system under consideration contains three individual components and two independent fluxes, i.e. that of the cation and that of the anion, which however are linked by the electroneutrality condition.

In electrodialysis the transport through the membranes must be considered. The system now consists of four components and thus three independent fluxes. Usually, the membrane is used as the frame of reference and in addition to the fluxes of the ions the flux of the solvent through the membrane must also be considered. The membranes used in electrodialysis usually carry positive or negative electrical charges and thus are permselective as far as the transport of ions is concerned, i.e. the cation-exchange membranes are preferentially permeable to cations and the anion-exchange membranes are preferentially permeable to anions. To meet the electroneutrality requirement the fluxes of cations and anions in the corresponding membrane must be equal and in opposite direction. The main difference in the ion fluxes in the membranes and in the solution
is the result of the difference in their transport number in the solution and in the membrane. In a strictly permselective anion-exchange membrane the current is transported by anions only and their transport number \( T_a^m \) is 1 and in a strictly permselective cation-exchange membrane the current is carried by cations only and their transport number \( T_c^m \) is 1. In the solution between the membranes the current is carried by both ions according to their mobility and their transport numbers are generally not very different.

In electrodialysis the solution between two membranes is well mixed providing a uniform concentration except for a thin boundary layer at the membrane surface with laminar flow. Under certain conditions this boundary layer may be considered as constant, and the mass transport through the layer can be described by a simple film model as will be shown later. When operated properly by providing good mixing of the bulk solution between the membranes and by limiting the current density to a certain maximum value the mass transport in the boundary layer is not rate limiting in electrodialysis for the transport of salt from a feed to a concentrate solution.

For a monovalent single electrolyte solution such as NaCl which is well mixed, so that boundary layer effects at the membrane surfaces can be neglected, the concentrations of cations and anions are equal and there is no concentration gradient in the solution. Under these assumptions the fluxes of the cations and the anions are equal, i.e. the number of cations transported through the cation exchange membrane are equal to the ions transported through the anion-exchange membrane. Thus, for a monovalent completely dissociated electrolyte such as NaCl the ion fluxes according to Equations (2.99) and (2.100) are:

\[
J_{\text{Cl}^-} = J_{\text{Na}^+} = J_S = \frac{2L_{\text{am}} \left( \frac{L_{\text{cm}}}{L_{\text{Na}^+}} - \frac{L_{\text{am}}}{L_{\text{Cl}^-}} \right)}{F \frac{d\phi}{dz} + RT \frac{d\ln a_s}{dz}}
\]

(2.121)

Here \( J_{\text{Na}^+} \) and \( J_{\text{Cl}^-} \) are the fluxes of Na\(^+\)-ions through the cation-exchange membrane and Cl\(^-\)-ions through the anion-exchange membrane; \( L_{\text{am}}^{\text{Na}^+} \) and \( L_{\text{cm}}^{\text{Cl}^-} \) are the phenomenological coefficients for the transport of Na\(^+\)- and Cl\(^-\)-ions through the corresponding membrane; \( J_S \) is the total salt transport from the feed solution to the concentrate solution.
Equation (2.121) describes the fluxes of the individual ions in electrodialysis as a function of an applied electrical potential gradient and an activity gradient. The activity gradient is proportional to the concentration difference between the concentrate and the diluate electrolyte solution.

To demonstrate the relevance of Equation (2.121) for the transport in electrodialysis it will be assumed that the concentration as well as the electrical potential gradients across the membranes are a linear function of their thickness and that the thickness of the cation-exchange and the anion-exchange membranes is equal. Thus is:

\[
J = J_{Na^+} = J_{Cl^-} = -2 \left( \frac{L_{am}^m L_{cm}^m}{L_{am}^m + L_{cm}^m} \right) F \left( \frac{\Delta \phi}{\Delta z} + \frac{RT \Delta \ln a_s}{F \Delta z} \right) \tag{2.122}
\]

\(\Delta \phi\) and \(\Delta \ln a_s\) are the differences in the electrical potential and the activities of the salt in the two solutions separated by the membranes, and \(\Delta z\) is the thickness of the membrane.

The term \(\frac{RT}{F} \Delta \ln a_s\) in Equation (2.122) represents an electromotive force and has the dimension of a potential. It is the potential established between solutions of different ion concentrations separated by a strictly permselective membrane.

In many practical applications of electrodialysis the concentration potential established between the diluate and concentrate solutions can be neglected. However, when large differences between the diluate and concentrate concentrations are required the concentration potential effects the overall process efficiency additionally by an osmotic water flow from the diluate to the concentrate solution.

**Water transport in electrodialysis**

Water transport in electrodialysis from the diluate to the concentrate process stream can effect the process efficiency significantly. If a convective flux as a result of pressure differences between flow streams can be excluded there are still two sources for the transport of water from the diluate to the concentrate solution. The first one is the result of osmotic pressure differences between the two solutions, and the second is the coupling of water to the ions being transported through the membrane due to the driving force of an electrical potential.
In the solution the flux of ions is generally described by using the solvent as frame of reference. If membranes are involved in the transport process they are generally used as frame of reference. Considering a system consisting of a single monovalent salt, a solvent and a membrane three independent fluxes are obtained, i.e. the cat- and anion flux and the water flux. The solvent flux through an ion-exchange membrane is the sum of two terms: (1) The osmotic water flux due to the solute concentration difference between the diluate and concentrate solutions and (2) the transport of solvent with the ions in the hydration shell. Each of the two terms may be dominating. In general, however, the pure osmotic solvent flux is much lower than the solvent transported by the hydration of the ions. In practice the solvent flux can be expressed by a solvent transport number which gives the number of moles of solvent transported by one mole of ions.

\[ T_{w}^{im} = \frac{n_w}{\sum n_i} \]  

Here \( T_{w}^{im} \) is the water transport number of an ion-exchange membrane, \( n_w \) refers to moles of water, and \( n_i \) to moles of ions.

The solvent transfer number depends on the membrane and on the electrolyte and its concentration. In aqueous salt solutions the water transport number is in the order of 10, i.e. one mole of ions transport ca. 10 moles of water through a typical commercial ion-exchange membrane. The water transport can effect the overall efficiency of electrodialysis significantly when feed solutions with high salt concentrations have to be demineralized as will be shown later.

**Membrane permselectivity**

Another parameter which is of importance in the practical application of electrodialysis is the membrane permselectivity which is defined for cation- and anion-exchange membranes by:

\[ \Psi_{mc} = \frac{T_{c}^{mc} - T_c}{T_a} \]  

and
Here $\psi$ is the permselectivity of a membrane, $T$ is the transport number, the superscripts mc and ma refer to cation- and anion-exchange membranes, and the subscripts c and a to cation and anion, respectively.

The permselectivity of an ion-exchange membrane relates the transport of electric charges by counterions to the total transport of electric charges through the membrane. An ideal permselective cation exchange membrane would transport positively charged ions only, i.e. for $T_c^{mc} = 1$ is $\psi^{mc} = 1$. The permselectivity approaches zero when the transport number within the membrane is identical to that in the electrolyte solution. For the anion-exchange membrane holds the corresponding relation.

2.4.3.4 Membrane mass transport in microfiltration

The principle of microfiltration is depicted in Figure 2.9. The membrane separating a feed solution from a permeate or filtrate has a symmetric porous structure with an average pore size between 0.1 to 10 $\mu$m.

The driving force is a pressure gradient and if the concentration of components in the two phases separated by the membrane is not identical there will also be a chemical potential gradient acting as driving force for the mass transport across the membrane. However, mass transport in microfiltration membranes takes place exclusively through the pores. The solid membrane matrix can generally be considered as completely impermeable. Both solvents and solutes permeate the membrane by viscous flow through the pores. There may also be diffusion in the moving pore liquid if concentration gradients are established between the feed and filtrate solutions. In microfiltration only large particles which have diameters in excess of ca. 0.1 $\mu$m are separated by the membrane. Therefore, the osmotic pressure difference between the feed and filtrate solution is negligibly low.
The diffusivities of the large particles in the pore liquid is also extremely low and the contribution of the diffusive flux to the overall mass transport across the membrane can generally be neglected. Thus, in microfiltration the viscous flow is dominating and the mass transport can be expressed by phenomenological Equation (2.64) which, however, is significantly simplified since all kinetic coupling of individual component fluxes and diffusion are neglected. The flux through a microfiltration membrane is given to a first approximation by:

$$J_v = \sum_k J_k \bar{v}_k \cong L_v \frac{dp}{dz} \cong L_v \Delta p$$  \hspace{1cm} (2.126)$$

Here \( J \) is the flux across the membrane, the subscripts \( v \) and \( k \) refer to volume and components in the solution, \( \bar{v} \) is the partial molar volume, \( p \) the pressure, and \( z \) a directional co-ordinate; \( L_v \) is a phenomenological coefficient referring to viscous flow, and \( \Delta p \) is the pressure difference between the feed and filtrate solution.

Expressing the phenomenological coefficient \( L_v \) in terms of the membrane and the solution properties, i.e. the pore size and porosity of the membrane and the solution viscosity, leads to Hagen-Poiseuille's law:
Here are $\varepsilon$ the membrane porosity, $r$ the pore radius, $\eta$ the viscosity, $\tau$ a tortuosity factor, $\Delta p$ the pressure difference across the membrane, and $\Delta z$ the membrane thickness. The tortuosity factor is defined as the ratio of the actual pore length to the thickness of the membrane taking into account that the pore length in general is somewhat longer than the cross-section of the membrane. Thus, is always $\tau > 1$ and the porosity $\varepsilon < 1$.

The flux through a microfiltration membrane is adequately described by Equation (2.127). Another parameter which is of interest for the practical application of microfiltration is the separation characteristic of a membrane. This is generally expressed by the retention or rejection of a certain size particle which is given by:

$$R_i = \left(1 - \frac{C_i^p}{C_i^f}\right)$$

(2.128)

Here $R$ is the rejection coefficient, $C$ is the concentration, the subscript $i$ refers to a given component $i$ in the feed and the permeate, the superscripts $f$ and $p$ refer to the feed and permeate solutions. $R$ is always $\leq 1$ and a function of the particle and the pore size and pore size distribution.

2.4.3.5 Membrane mass transport in ultrafiltration

In ultrafiltration the driving force again is a pressure gradient and the mass transport is also dominated by the convective flux through pores. The principle of the process is depicted in Figure 2.10.
Fig. 2.10 Schematic drawing illustrating the principle of ultrafiltration

As in microfiltration a porous membrane is separating a feed solution from a permeate or filtrate. However, the structure of an ultrafiltration membrane is asymmetric having the smallest pores on the surface facing the feed solution and its pores are significantly smaller than those of a microfiltration membrane. Their diameters at the feed side surface of the membrane are between 2 and 10 nm. Since ultrafiltration membranes retain also some relatively low molecular weight solutes a concentration difference for the retained components between the feed and the permeate will be established, which in turn can lead to osmotic pressure differences and considerable diffusive fluxes of the solutes across the membrane. However, both viscous flow and diffusion occur in the pores while the solid matrix is completely impermeable. In ultrafiltration the flux can be expressed as a function of a hydrostatic pressure and a concentration difference between the feed and filtrate solutions by the phenomenological Equation (2.64). Generally, a kinetic coupling between the flux of individual components can be neglected and the volume flux can be described by:

\[ J_v = \sum_k L_k \bar{V}_k \frac{d\mu_k}{dz} + L_v \frac{dp}{dz} \]  

(2.129)

Here \( L \) is a phenomenological coefficient referring to interactions of the permeating components with the membrane matrix, \( \bar{V} \) is the partial molar volume, \( \mu \) is the chemical potential, \( p \) is the...
pressure, \( z \) is a directional co-ordinate, and the subscripts \( v \) and \( k \) refer to viscous flow and individual components of the feed solution. The first term in Equation (2.129) describes the diffusive fluxes of all components in the pores of the membrane and the second term the viscous flow.

Introduction of the relation for the chemical potential of the various components in the solution leads to:

\[
J_v = \sum k \bar{v}_k \left( \bar{v}_k p + RT \ln a_k \right) + L_v \frac{dp}{dz} \tag{2.130}
\]

In ultrafiltration the total flux in a dilute solution can be expressed to a first approximation by the flux of the solvent, i.e. \( J_v = J_w \) and the activity of the solvent in the solution \( a_w \) can be expressed by an osmotic pressure according to Equation (2.30). Assuming, furthermore, a linear relation for the pressure and activity gradients across the membrane integration of Equation (2.130) gives the flux of an ultrafiltration membrane as a function of pressure difference between feed and permeate solution, the hydrodynamic permeability for the viscous flow, the osmotic pressure difference between feed and permeate solution, and the phenomenological coefficient determining the diffusive flow of water through the membrane pores:

\[
J_v \approx J_w = L_w \bar{v}_w \left( \bar{v}_w \frac{\Delta p - \Delta \pi}{\Delta z} \right) + L_v \frac{\Delta p}{\Delta z} \tag{2.131}
\]

In most practical applications of ultrafiltration the first term of Equation (2.131) can be neglected since \( L_w \ll L_v \) and the difference in osmotic pressure between the feed and permeate solution is negligibly small compared to the hydrostatic pressure difference since generally only macromolecular components are retained. Thus the flux in ultrafiltration is given to a first approximation by:

\[
J_v = L_v \frac{\Delta p}{\Delta z} \tag{2.132}
\]
Considering the transport of solutes through an ultrafiltration membrane with high rejection capabilities the diffusive flux can often not be neglected. The flux of the solute \( s \), can be expressed by the phenomenological Equation (2.64) which can be modified due to the assumption that no coupling of individual component fluxes occurs:

\[
J_s = L_s \frac{d\mu_s}{dz} + L_{vs} \frac{dp}{dz}
\]  

Here \( L_s \) and \( L_{vs} \) are the phenomenological coefficients relating the flux of the component \( k \) to the chemical potential and to the pressure gradient, respectively.

The phenomenological coefficient \( L_{vs} \) expresses the transport of the component \( s \) coupled with the viscous flow. The coefficient \( L_{vs} \) can also be expressed by the coefficient \( L_v \) multiplied by the concentration of the component \( k \) in the pore fluid \( C^m_s \). Introducing furthermore, the relation for the chemical potential into Equation (2.133) leads to:

\[
J_s = L_s \frac{d\nu_s p + RT \ln a_s}{dz} + L_v C^m_s \frac{dp}{dz}
\]  

It can be shown that for hydrostatic pressure differences usually applied in ultrafiltration is: \( \nu_s p << RT \ln a_s \). If it is assumed that to a first approximation the activity coefficient of the solutes in the membrane is 1, the phenomenological coefficient can be expressed by the Fick's diffusion coefficient according to Equation (2.86). Introducing these approximations into Equation (2.134) leads to:

\[
J_s = J v C^m_s - D^m_s \frac{dC^m_s}{dz}
\]  

Integration of Equation (2.135) over the length of the pores gives:
Here $J_v$ is the flux, $C$ is the concentration, $D$ the diffusion coefficient, $\tau$ the tortuosity factor, and $\Delta z$ the thickness of the membrane; the subscript $s$ refers to the component $s$ and the superscripts $m$, ('), and (") refer to the membrane and the feed and the filtrate solution.

Equation (2.136) shows that the flux of a component $s$ which is partly retained by the membrane in ultrafiltration consists of two terms. The first term represents the viscous flow and is a linear function of the hydrostatic pressure. The second term represents the diffusion in the pore liquid and is an exponential function of the hydrostatic pressure.

The retention of an ultrafiltration membrane for a component $k$ can be described as a function of the hydrostatic pressure and the partition coefficients of the component $k$ between the membrane and the feed and permeate solutions by introducing Equation (2.136) into Equation (2.128).

The effect of the hydrostatic pressure on the retention in ultrafiltration becomes more clear when two extreme cases are considered, i.e. a very large and a very small hydrostatic pressure differences between the feed and the permeate solution. At large pressure differences the viscous flux is high and the retention approaches a maximum value which is determined by the distribution coefficient of the solute between the membrane and the solution.

2.4.3.6 Membrane mass transport in reverse osmosis

In reverse osmosis the driving force is also a hydrostatic pressure difference. The principle of the process is illustrated in Figure 2.11 which shows a solution containing a low molecular weight component separated by an membrane from the solvent and a hydrostatic pressure difference applied across the membrane resulting in a flux of solvent from the solution into the pure solvent.
The membrane used in reverse osmosis has an asymmetric structure with a dense barrier layer at the side facing the feed solution. It is assumed that in this layer this transport of individual components is by diffusion and that viscous flow through pores or pinholes can be neglected. For describing the transport in reverse osmosis membranes the so-called solution-diffusion transport mechanism can be assumed which relates the permeability of a component to the product of its solubility and its mobility in the membrane matrix. The hydrostatic pressure driving force applied in reverse osmosis does not result in a viscous flow but in an change of the chemical potential of the individual components. Thus, the driving force for the mass transport in reverse osmosis is the gradient in the chemical potential of the individual components. The mass transport in reverse osmosis can be described by the so-called solution-diffusion model or by the phenomenological Equation (2.64).

*Description of the mass transport in reverse osmosis by the phenomenological equations*

In a reverse osmosis system which consists of a membrane and a two component feed solution, i.e. a solvent and a solute two independent fluxes will be obtained when the membrane is used as frame of reference. These fluxes can be described by:
\[ J_1 = L_{11} \text{grad} \mu_1 + L_{12} \text{grad} \mu_2 \]  
\[ J_2 = L_{21} \text{grad} \mu_1 + L_{22} \text{grad} \mu_2 \]  

Considering transport only in direction perpendicular to the membrane surface and introducing water as component 1 and salt as component 2 the Equations (2.137) and (138) become:

\[ J_w = -L_w \frac{d\mu_w}{dz} - L_{ws} \frac{d\mu_s}{dz} \]  
\[ J_s = -L_{sw} \frac{d\mu_w}{dz} - L_s \frac{d\mu_s}{dz} \]  

Here \( J_w \) and \( J_s \) are the water and salt fluxes through the membrane, \( L_w, L_s, L_{ws} \) and \( L_{sw} \) are phenomenological coefficients, \( \frac{d\mu_w}{dz} \) and \( \frac{d\mu_s}{dz} \) are the gradients in the chemical potentials of the water and the salt across the membrane from the high pressure to the low pressure side.

Assuming a linear relation of the chemical potential gradients across the membrane and applying the dissipation function which postulates positive values for \( L_w \) and \( L_s \) and neglecting any kinetic coupling between individual fluxes Equations (2.139) and (2.140) can be re-written as:

\[ J_w = -L_w \Delta \mu_w \]  
\[ J_s = -L_s \Delta \mu_s \]  

Introducing the chemical potential as function of pressure and composition, i.e. Equation (2.27) leads to:

\[ J_w = -L_w \left( \mu_{w}^p - \mu_{w}^f \right) = -L_w \left[ V_w \left( p^p - p^f \right) + RT \left( \ln a_w^p - \ln a_w^f \right) \right] \]

and
\[ J_s = -L_s \left( \mu_s^p - \mu_s^f \right) = -L_s \left[ \nabla_s \left( p^p - p^f \right) + RT \left( \ln a_s^p - \ln a_s^f \right) \right] \]  \hfill (2.144)

Here \( \nabla_w \) and \( \nabla_s \) are the partial molar volumes of the water and the salt and the superscripts \( p \) and \( f \) refer to feed and permeate solution.

Introducing the osmotic pressure into Equations (2.143) and (2.144) which is given in reference to the water activity by:

\[ \pi = \frac{RT}{\nabla_w} \ln a_w \]  \hfill (2.145)

and for highly dilute solutions by:

\[ \pi = \frac{RT}{C_s} \ln a_s \]  \hfill (2.146)

leads to:

\[ J_w = -L_w \nabla_w \left( \Delta p - \Delta \pi \right) \]  \hfill (2.147)

and

\[ J_s = -L_s \left( \nabla_s \Delta p + \frac{\Delta \pi}{C_s} \right) \]  \hfill (2.148)

Equations (2.147) and (2.148) describe the salt and water flux in reverse osmosis under the assumption that there is no kinetic coupling between the water and the salt flux, i.e. the cross coefficient \( L_{ws} \) is zero. This, however, is only correct to a first approximation. For a correct description of the transport in reverse osmosis the cross-coefficient should be considered. However, the coefficients \( L_w \) and \( L_s \) and the cross coefficient \( L_{ws} \) are not so easily determined experimentally in independent measurements. But there is a possibility to convert these coefficients in experimentally accessible constants when the phenomenological equations are slightly modified.

Usually in reverse osmosis the total volume flux is measure. It is therefore possible to consider a volume flux \( J_V \) and a diffusive flux \( J_D \) which are given by:
\[ J_v = J_w \nabla_w + J_s \nabla_s \]  \hspace{1cm} (2.149)

and

\[ J_D = \frac{J_s}{C_s} - \nabla_w J_w \]  \hspace{1cm} (2.150)

Introducing Equations (2.147) to (2.150) into the dissipation function and re-arranging leads to:

\[ \Psi = J_w \Delta \mu_w + J_s \Delta \mu_s = (J_w \nabla_w + J_s \nabla_s) \Delta p + \left( \frac{J_s}{C_s} - \nabla_w J_w \right) \Delta \pi \]  \hspace{1cm} (2.151)

and

\[ \Psi = J_v \Delta p + J_D \Delta \pi \]  \hspace{1cm} (2.152)

The first term in Equation (2.151) describes the total volume flux \( J_v \) as function of the applied pressure and the second term describes the diffusion flux of the salt \( J_D \) relative to that of the water.

This leads to a new set of phenomenological equations given by:

\[ J_v = L_p \Delta p + L_{pD} \Delta \pi \]  \hspace{1cm} (2.153)

and

\[ J_D = L_{pD} \Delta p + L_D \Delta \pi \]  \hspace{1cm} (2.154)

For the new set of Equations the boundary conditions according the thermodynamic of irreversible processes are: \( L_p \) and \( L_D > 0 \) and \( L_{pD} = L_{DP} \).

By applying different experimental conditions the Equations (2.153) and (2.154) allows some characteristic phenomena in reverse osmosis to be elucidate and to derive coefficients that can be experimentally determined.

Assuming that there is no pressure difference, i.e. \( \Delta p = 0 \), then the diffusive flux is then given by:

\[ (J_D)_{\Delta p=0} = L_D \Delta \pi \]  \hspace{1cm} (2.155)
and the volume flux by:

\[(J_v)_{\Delta p=0} = L_{pD}\Delta\pi \]  \hspace{1cm} (2.156)

Assuming that there is no the osmotic pressure difference, i.e. \(\Delta\pi = 0\), then the diffusive flux is given by:

\[(J_D)_{\Delta\pi=0} = L_{Dp}\Delta p \]  \hspace{1cm} (2.157)

and the volume flux by:

\[(J_v)_{\Delta\pi=0} = L_p\Delta p \]  \hspace{1cm} (2.158)

Here the coefficient \(L_p\) relates the hydrodynamic flux to a pressure difference, the coefficient \(L_D\) relates the diffusive flux to an activity gradient expressed by the osmotic pressure, the coefficient \(L_{pD}\) relates the hydrodynamic flux to an activity gradient and the coefficient \(L_{Dp}\) describes the diffusive flux as the result of pressure difference. According to the Onsager relation \(L_{pD}\) and \(L_{Dp}\) must be equal.

\[ \left( \frac{J_v}{\Delta\pi} \right)_{\Delta p=0} = L_{pD} = L_{Dp} = \left( \frac{J_d}{\Delta p} \right)_{\Delta\pi=0} \]  \hspace{1cm} (2.159)

A further useful information is obtained considering a hydrostatic pressure difference at zero volume flux, i.e. the osmotic equilibrium:

\[ (\Delta p)_{v=0} = -\frac{L_{pD}}{L_p} \Delta\pi = \sigma \Delta\pi \]  \hspace{1cm} (2.160)

Here \(\sigma\) is the so-called Staverman reflection coefficient which is a measure for the permselectivity of a membrane.

Equation (2.160) shows that in osmotic equilibrium the hydrostatic pressure difference between to solution separated by a membrane is equal to the osmotic difference if \(L_p = L_{pD}\) and therefore...
σ =1. This is only the case for a strictly semipermeable membrane. Usually, the Staverman reflection coefficient has values between 0 and 1.

Introducing Equation (2.160) into Equations (2.153) and (2.150) leads to:

\[ J_v = L_p (\Delta p - \sigma \Delta \pi) \quad (2.161) \]

and

\[ J_s = C_s (1 - \sigma) J_v + \omega \Delta \pi \quad (2.162) \]

Here \( \omega \) is the permeability of the salt which is given by:

\[ \left( \frac{J_s}{\Delta \pi} \right)_{J_v=0} = \omega = \frac{C_s}{L_p \frac{L_D}{L_{pD}}} \quad (2.163) \]

Based on the phenomenological equations the mass transport in reverse osmosis assuming a solution of a single salt can be described by three coefficients, i.e. \( L_p \) the hydrodynamic permeability of the membrane, \( \omega \) the salt permeability and \( \sigma \) the reflection coefficient. All three coefficients can experimentally be measured.

**Description of the mass transport in reverse osmosis by the solution-diffusion model**

The solution-diffusion model describes the flux of different components through a membrane by the product of its concentration and mobility in the membrane. Applied to reverse osmosis the flux of a component \( i \) is given by:

\[ J_i = C_i m_i \mu_i d \frac{d}{dz} \quad (2.164) \]

Introducing the gradient in the chemical potential of the component \( i \) as a function of its activity and the pressure from Equation (2.27) leads to:

\[ J_i = C_i m_i \frac{1}{d} \left( \gamma_i dp + RT d \ln a_i \right) \quad (2.165) \]
The mobility of a component $i$ in the membrane can be directly be related to Fick's diffusion coefficient in the membrane as follows. At constant pressure and temperature is the flux of a component $I$ given by:

$$\left( J_i \right)_{pT} = C_i^m m_i^m RT \frac{d \ln a_i}{dz} = C_i^m m_i^m RT \frac{d \ln \gamma_i C_i}{dz} \quad (2.166)$$

If it is assumed that the activity coefficient $\gamma_i$ of the component $i$ in the membrane is to a first approximation 1 and that concentration in the membrane $C_i$ is a linear function of the distance $z$, then Equation (2.166) can be rewritten as:

$$\left( J_i \right)_{pT} = C_i^m m_i^m RT \frac{d \ln C_i}{dz} = C_i^m m_i^m RT \frac{d \ln C_i}{dz} = C_i^m m_i^m RT \frac{d C_i}{C_i dz} = -m_i^m RT \frac{\Delta C_i}{\Delta z} \quad (2.167)$$

Comparing Equation (167) with Fick's law of diffusion which is given by:

$$J_i = -D_i^m \frac{\Delta C_i^m}{\Delta z} \quad (2.168)$$

results in a relation between the Fick's diffusion coefficient and the mobility of a component in the membrane under ideal conditions for a two component system. Thus is:

$$m_i^m RT = D_i^m \quad (2.169)$$

Introducing Equation (2.169) into Equation (2.165) leads to:

$$J_i = C_i^m D_i^m \frac{1}{RT} \frac{d}{dz} \left( V_i dp + RT d \ln a_i \right) \quad (2.170)$$
The concentration of a component in the membrane can be related to its concentration in the adjacent solutions by a distribution or partition coefficient \( k_i \). Thus is:

\[
C_i^m = k_i C_i
\]  
(2.171)

For a dilute solution it can be assumed that:

\[
C_w \bar{v}_w = 1
\]  
(2.172)

Introducing Equations (2.171) and (2.172) into Equation (2.170) gives the solute and the water flux in reverse osmosis as a function of the diffusion coefficient, the partition coefficient, the hydrostatic pressure driving force and the solute concentration in the feed and permeate solutions.

\[
J_v = \frac{k_s D_s^{m}}{RT \Delta z} (\Delta p - \Delta \pi)
\]  
(2.173)

and

\[
J_s = -k_s D_s^{m} \frac{C_p^m - C_s^f}{\Delta z}
\]  
(2.174)

Here \( J_v \) is the volume flux, \( J_s \) is the solute flux, \( D \) is the diffusion coefficient, \( k \) is the distribution coefficient of components between the membrane and the adjacent solutions, \( C \) is the concentration, \( p \) the hydrostatic pressure, \( z \) the directional coordinate perpendicular to the membrane surface, and \( \pi \) the osmotic pressure of the solutions, the subscripts \( s \) and \( w \) refer to solute and water, respectively, and the superscripts \( m \), \( p \), and \( f \) refer to membrane, feed and permeate, respectively.

Also the Equations (2.173) and (2.174) contain several assumptions they do describe the mass transport in reverse osmosis membranes quite well and are commonly used in practical applications.
2.4.3.7 Membrane mass transport in pervaporation
Pervaporation is a membrane process in which the permeation of certain components through a membrane from a liquid feed mixture into a gas phase is combined with the evaporation of these components. The principle of the process is illustrated in Figure 2.12. The membranes used in pervaporation have generally an asymmetric structure similar to that used in reverse osmosis with a thin skin consisting of homogeneous material, e.g. a polymer, in which the different components are transported according to their solubility and their diffusivity. The driving force for the transport is the chemical potential gradient of the permeating components in the membrane. The chemical potential gradient in the membrane can be related to the activities of the components in the liquid and their fugacities in the vapor phase, which are proportional to the partial vapor pressure in the liquid and vapor. To establish a partial pressure difference of a component in the liquid and the vapor phase, generally, a vacuum is applied at the permeate side of the membrane. But differences in the partial pressure of a component can also be established by using a sweeping gas on the permeate side or by a temperature difference between the liquid feed and the vapor.

![Asymmetric membrane with a dense "skin" layer](image)

Fig. 2.12 Schematic drawing illustrating the principle of pervaporation showing an asymmetric membrane with a dense solution-diffusion-type barrier layer
The transport of a component through a pervaporation membrane consists of three consecutive steps: 1. Sorption of the component from the liquid feed into the membrane material, 2. diffusion of the dissolved component through the membrane matrix and 3. desorption of the component from the membrane into the vapor phase.

The separation of various components from a liquid mixture is not only determined by differences in their vapor pressure but also by their permeation rate through the membrane. The actual driving force for the permeation of the different components through the membrane is their chemical potential difference between the two phases separated by the membrane. The chemical potential difference between the two phases is inducing a concentration gradient within the membrane as indicated in Figure 2.13 which shows schematically the different steps of the mass transport through a pervaporation membrane.

![Diagram of mass transport through a pervaporation membrane](image)

Fig. 2.13 Mass transport through a solution diffusion membrane in pervaporation

It can be assumed that there is neither viscous flow nor kinetic coupling of the fluxes of individual components. The flux of a component k can then be expressed according to Equation (2.64) by:
Introducing the pressure and activity dependence of the chemical potential leads to:

$$J_k = L_k \frac{d\mu_k}{dz} \quad (2.175)$$

Here $J$ is the flux through the membrane, $L$ is the phenomenological coefficient, $\nu$ the partial molar volume, $p$ the hydrostatic pressure, and $a$ the activity; the subscript $k$ is referring to the component $k$.

The term $\nu kp$ can generally be neglected since for hydrostatic pressures typically applied in pervaporation it is: $\nu kp \ll RT \ln a_k$.

Since in pervaporation the feed mixture is a liquid and the permeate is a gas it is convenient to express the activity gradient of the individual components in terms of their fugacity or the partial vapor pressure. Assuming equilibrium between the two phases and the membrane the activity of the component $k$ in the membrane at the side facing the liquid is:

$$a_k^m' = a_k^m = X_k^m \gamma_k = \frac{p_k^\phi_k}{p_k^o}$$

and that at the side facing the vapor is:

$$a_k^m'' = \frac{p_k^\phi_k}{p_k^o}$$

Here $X_k$ is the molar fraction, $\gamma_k$ is the activity coefficient in the liquid, $\phi_k$ is the fugacity coefficient in the vapor, and $p_k$ is the partial pressure of the component $k$, the superscripts $m$, ('), and ('') refer to membrane, feed liquid, and vapor permeate, $p_k^o$ is the saturation pressure of the component $k$ at a given temperature.

Introducing Equations (2.177) and (178) into Equation (2.176) and integrating across the membrane leads to:
respectively:

\[ J_k = \frac{L_k RT}{a_k^m} \frac{1}{p_k^o} \frac{p_k^{\phi_k} - p_k^{\phi_k^o}}{\Delta z} \]  

(2.179)

The phenomenological coefficient can be related to the diffusion coefficient and the average activity of the component \( k \) in the membrane to its molar fraction in the membrane:

\[ a_k^m = X_k^m \gamma_k^m \]  

(2.181)

and

\[ D_k^m = \frac{L_k RT}{X_k^m} \]  

(2.182)

Introducing Equations (2.181) and (2.182) into Equation (2.180) leads to:

\[ J_k = \frac{L_k RT}{a_k^m} \frac{1}{p_k^o} \frac{p_k^{\phi_k} - X_k^{\gamma_k^o} p_k^o}{\Delta z} \]  

(2.183)

Here \( D_k^m \) is the diffusion coefficient of the component \( k \) in the membrane, \( k_k^* \) is the distribution coefficient of the component \( k \) between the membrane and the outer phases which is given by:

\[ k_k^* = \frac{1}{p_k^o p_k^m} \]  

(2.184)

Equation (2.184) describes the permeation flux of a component \( k \) as a function of the feed and permeate mixture composition and its diffusivity and solubility in the membrane which can easily be determined by independent measurements. The practical application of Equation (2.183), however, is rather limited since the diffusion coefficient as well as the distribution coefficient are not constant but depend strongly on the concentration of the permeating
component in the membrane. This dependency must be determined experimentally and may be different for different membrane materials and vapors.

The product of diffusion and distribution coefficient is referred to as permeability coefficient, and the ratio of the permeability coefficients of two components determine the membrane selectivity for the two components.

\[ D_{jk} = P_k \]  
\[ S_{jk} = \frac{P_j}{P_k} \]

Here P is the permeability of the membrane, S is the membrane selectivity, and j and k refer to the components of the mixture.

The separation achieved in practical pervaporation experiments is expressed in a separation factor which for a mixture consisting of two components is defined as:

\[ \alpha_{j,k} = \frac{X_j' X_k'}{X_j X_k} \]

Here \( \alpha_{j,k} \) is the separation factor for the two components j and k, X is the molar fraction and (') and ('') refer to the feed and the permeate.

The membrane selectivity and the separation factor are defined as \( S > 1 \) and \( \alpha > 1 \). The separation factor \( \alpha \) depends on membrane properties, i.e. the membrane selectivity S, as well as on experimental conditions as can be shown by combination of Equations (2.185) (2.186) and (2.187) and introducing the two following relations: \( \frac{X_j'}{X_k} = \frac{J_j}{J_k} \) and \( P_k = X_k p \). Thus is:

\[ \alpha_{j,k} = S_{j,k} \frac{X_j' \phi_j p_j' - X_j' \gamma_j p_j'}{X_k \phi_k p_k' - X_k \gamma_k p_k'} \]  
\[ \frac{X'}{X} \]

(2.188)
Here $\alpha$ is the separation factor, $S$ the membrane selectivity, $X$ the molar fraction, $p$ the pressure, $f$ the activity and $\phi$ the fugacity coefficient, the subscripts $j$ and $k$ refer to components of the mixture, and the superscripts $o$, $(')$ and $"$ refer to saturation pressure, feed and permeate, respectively.

In pervaporation the partial pressure of the components on the permeate side is kept as low as possible by either using a sweeping gas or more commonly by applying a vacuum, i.e., $X_{j}'\phi_{j}p' << X_{j}'\gamma_{j}p^{o}$ and $X_{k}'\phi_{k}p'' << X_{k}'\gamma_{k}p^{o}$. For a pervaporation experiment using a vacuum the separation factor is to a first approximation:

$$\alpha_{j,k} = S_{j,k} \frac{\gamma_{j}p^{o}_{j}}{\gamma_{k}p^{o}_{k}}, \lim_{p'' \to 0} \theta 0$$ \hspace{1cm} (2.189)

It should be noticed that the separation factor consists of two terms, the first term, i.e. $S_{j,k}$ represents the membrane selectivity and the second term $\frac{\gamma_{j}p^{o}_{j}}{\gamma_{k}p^{o}_{k}}$ the thermodynamic liquid/vapor equilibrium which represents the separation that would be achieved by distillation. In pervaporation the membrane selectivity can increase or decrease the distillation selectivity and eventually pushing the over all separation factor into the opposite direction.

2.4.3.8 Membrane mass transport in gas separation

The principle of gas separation is illustrated in Figure 2.14, which shows two different gas mixtures separated by a membrane. The driving force for the gas to permeate the membrane is a pressure gradient.
In gas separation both porous and dense membranes are used as selective barriers. In porous membranes the transport of gases is based on the so-called Knudsen diffusion. Knudsen diffusion can be considered as viscous flow in narrow pores, i.e. pores with a diameter that is smaller than the mean free path length of the diffusing gas molecules. The mean free path length is defined as the average distance a gas molecule travels before it will collide with an other gas molecule. The mean free path length of a gas molecule depends on the nature of the gas, the temperature, and the pressure. It is given by:

\[
\lambda = \frac{kT}{\pi d_{\text{gas}} p \sqrt{2}}
\]  \hspace{1cm} (2.190)

Here \( \lambda \) is the mean free path length of a gas molecule, \( k \) is the Bolzmann constant, \( d_{\text{gas}} \) the diameter of the gas molecule, and \( p \) is the hydrostatic pressure.
The difference between viscous flow and Knudsen diffusion is illustrated in Figure 2.15. This figure shows two membrane pores of different diameter with a certain number of gas molecules.

![Viscous Flow and Knudsen Diffusion](image)

**Fig. 2.15 Schematic drawing illustrating viscous flow and Knudsen diffusion**

The mean free path length of gases at room temperature and atmospheric pressure is in the order of a couple of nanometers. This means that only membranes with a mean pore size below a couple of nanometers can separate gases due to a Knudsen diffusion mechanism.

The flux in Knudsen diffusion is given by:

$$J_i = \frac{\pi n r^2 D_i^k \Delta p}{RT \tau \Delta z}$$

\hspace{1cm} (2.191)

The Knudsen diffusion coefficient is given by:

$$D_i^k = 0.66 r \sqrt{\frac{8RT}{\pi M_w}}$$

\hspace{1cm} (2.192)

Equation (2.192) shows that the Knudsen diffusion coefficient of a gas molecule is inverse proportional to the square root of its molecular weight. Thus, the separation of two gases based on Knudsen diffusion is given by the ration of square root of the molecular weights.

Separation of gases can be achieved in microporous as well as in homogeneous membranes. The selectivity of microporous membranes for different membranes is because of the Knudsen diffusion transport mechanism in general rather low and to a first approximation proportional to the square root out of the molecular weight ratios of the different components. Significantly higher selectivity can be obtained in homogeneous membranes, where the transport mechanism is based on the solution and diffusion of the various components within the membrane phase.
The mass transport in a so-called solution-diffusion membrane is illustrated in Figure 2.16. It consists of three relevant steps:

1. Sorption of the various components from a feed mixture according to their partition coefficient between the gas and polymer phase;
2. diffusion of the individual components within the membrane phase according to their activity gradients; and
3. desorption of the components from the membrane in the permeable gas phase.

![Fig. 2.16 Schematic diagram illustrating the three-step transport mechanism in solution-diffusion type membranes](image)

The driving force for the mass transport of gases in solution-diffusion type membranes is the activity gradient of the permeating components within the membrane phase which can be related to the component’s partial pressures in the feed mixture and in the permeate. According to Equation (2.64) the flux of a component in gas separation in a membrane without viscous flow and no coupling of fluxes is given by:

\[ J_k = L_k \text{grad} \mu_k^m \]  

(2.193)

Here \( \mu_k^m \) is the chemical potential of the component \( k \) in the membrane and \( L_k \) is the phenomenological coefficient.

The chemical potential of a component in the membrane is identical to at the interface between the membrane and the adjacent outer phases, i.e., equilibrium is assumed between the membrane and the outer phase.
The chemical potential gradient of a component \( k \) in the membrane is given by:

\[
\frac{d\mu_k^m}{dz} = RT \frac{d\ln a_k^m}{dz} = \frac{RT \, da_k^m}{a_k^m \, dz} = \frac{RT \, \Delta a_k^m}{\Delta z}
\] (2194)

Relating the chemical potential gradient of a component within the membrane phase to its partial pressure in the outside phase leads to:

\[
\Delta a_k^m = \frac{\Delta p_k \phi_k}{p_k}\n\] (2.195)

Here \( \phi_k \) is the fugacity coefficient of the component \( k \) in the outside mixtures, \( p_k \) is the partial pressure and \( p_k^o \) is a standard pressure value of the component \( k \).

Introducing Equations (2.194) and (2.195) into Equation (2.193) leads to:

\[
J_k = -L_k \frac{RT}{a_k^m p_k^o} \frac{\Delta p_k \phi_k}{\Delta z}
\] (2.196)

The phenomenological coefficient can be related to the Fick's diffusion coefficient as was shown earlier by:

\[
D_k^m = L_k \frac{RT}{C_k^m}
\] (2.197)

and

\[
k_k = \frac{1}{\gamma_k^m p_k^o}
\] (2.198)

Here \( k_k \) is the partition coefficient describing the solubility of the component \( k \) in the membrane material and \( \gamma_k^m \) is the activity coefficient of the component \( k \) in the membrane.

Introducing the relation between the phenomenological coefficient \( L_k \) and the diffusion coefficient and the partition coefficient, i.e. Equations (2.197) and (2.198) into Equation (2.196) leads to:

\[
J_k = -D_k^m k_k \frac{p_k^o \phi_k^{'} - p_k^{'} \phi_k^{'}}{\Delta z} = -p_k \frac{p_k^o \phi_k^{''} - p_k^{''} \phi_k^{'}}{\Delta z}
\] (2.199)

Here ('') and ('''') refer to the feed mixture and the permeate, respectively, and the product of diffusion and partition coefficient is the permeability coefficient.
\[ P_k = D_m^k k_k \]  

Here \( P_k \) is the membrane permeability for the component \( k \).

In deriving Equation (2.199) for the mass transport in solution-diffusion membranes it is assumed that the sorption and desorption is fast compared to the diffusion in the membrane and that equilibrium is achieved at the interfaces. Furthermore, kinetic coupling of the fluxes of the diffusing components in membranes is neglected. It should also be noted that the diffusion coefficient and the solubility coefficient are functions of the temperature and the concentrations of the components in the membrane. Especially in permeation of organic vapors, the diffusion coefficient may vary by several orders of magnitude with the concentration of the permeating components.

For the relationship between the diffusion coefficient and the concentration of the diffusing component different equations accounting for dual sorption or free volume and structural changes of the polymer are discussed in the literature. It should be pointed out that in gas and especially vapors permeation it is generally not possible to predict the mass transport behavior of various components in a mixture from single component measurements.

For a practical application the separation efficiency of the membrane is a crucial parameter. In gas permeation the separation efficiency of a membrane is expressed by its selectivity and/or its separation factor. The selectivity of a membrane for various components of a mixture is defined by the ratio of the permeability. For a binary mixture with the components \( i \) and \( j \), the selectivity is:

\[ S_{j,k} = \frac{P_j}{P_k} \]  

Here, \( S_{j,k} \) is the permeation selectivity of a membrane for the components \( i \) and \( k \), and \( P_k \) and \( P_j \) are their permeabilities.

According to Equation (2.200) the permeation selectivity can be split into two terms:

\[ S_{j,k}^P = S_{j,k}^D S_{j,k}^S \]  

Here, \( S_{j,k}^D \) and \( S_{j,k}^S \) are respectively the diffusivity and solubility selectivity of a membrane for the components \( k \) and \( j \).
The selectivity is a useful parameter to characterize a membrane. For the design of a membrane plant, however, the separation factor is more useful. For a binary mixture the separation factor is defined by:

$$\alpha_{jk} = \frac{X_j' X_k'}{X_j X_k}$$

Here \(\alpha\) is the separation factor and \(X\) is the mole fraction, the subscripts \(k\) and \(j\) refer to the two components, and the superscripts \('\) and \(''\) refer to the feed and the permeate.

The separation factor is defined to be always \(> 1\). It is related to the membrane selectivity by:

$$\alpha_{jk} = S_{j,k} \frac{X_j' \phi_j' p''}{X_j' \phi_j' p'' - X_k' \phi_k' p''}$$

\(\alpha\) is the separation factor, \(S\) is the selectivity for a binary mixture, \(p\) is the pressure and the partial pressure, respectively, \(\phi\) is the fugacity coefficient and \(X\) is the mole fraction. The superscripts \('\) and \(''\) refer to the feed and the permeate, and the subscripts \(k\) and \(j\) to the components in the mixture.

For an infinitely small ratio of permeate to feed pressure, i.e., \(\lim p''/p' > 0\), the separation factor becomes identical with the selectivity times the ratio of the fugacity coefficients in the feed mixture:

$$\alpha_{jk} = S_{j,k} \frac{\phi_j'}{\phi_k'}$$

In vapor and gas separation \(\alpha\) is normally functions of the feed concentration.

2.5 Energy requirements in membrane processes

The energy required in membrane processes is an additive of two terms: (1) The energy to transfer the components from feed mixture through a membrane into permeate mixture and (2) the energy required to pump the solutions through the membrane apparatus. The second term can easily be calculated from the pressure loss, which is obtained in the various flow streams pumped through the membrane containing apparatus. The pressure loss shall here not further be discussed.

The energy required for separating different components permeation through a membrane consists of two parts. The first part is the reversible energy given by the Gibb's free energy of
mixing obtained when the retentate and permeate solutions are mixed. It is the minimum energy required in any separation process. The second part is the energy required for "dragging" the individual components through a membrane under a given driving force. This energy is used to overcome the friction between the transported components and the membrane matrix. It is irreversible loss.

2.5.1. Minimum energy required for the separation of a molecular mixture

In membrane separation processes as in any other separation processes the minimum work that is required for the separation of various components from a mixture is given by Gibb's free energy of mixing the two separated solutions. For a solution which consists of one or more components the Gibb’s free energy of mixing is given by:

$$
\Delta G_m = G' - G'' = \sum_i (\mu'_i dn'_i = \mu''_i dn''_i) \equiv RT \sum_i \Delta n_i \ln \frac{a'_i}{a''_i}
$$

(2.206)

Here $\Delta G_m$ is the Gibb’s free energy of mixing two solutions indicated by ‘ and “, $\mu$ is the chemical potential, a the activity and n the number of moles, the subscript i refers to individual components.

For filtration processes such as reverse osmosis the energy requirement for the for removing the solvent from the solution can be expressed by the difference in the osmotic pressure of the two solutions. If it is assumed that the membrane is permeable for the only solvent then the Gibb’s free energy can be expressed by chemical potential of the solvent, which is related to the osmotic pressure of the solutions by:

$$
\pi = \frac{RT \ln a_w}{V_w}
$$

(2.207)

Here the subscript w refers to the solvent, e.g. water.

Introducing Equation (2.207) into Equation (2.206) leads to:

$$
\Delta G_m = \Delta n_w V_w \Delta \pi \approx V_f \Delta \pi
$$

(2.208)
Here $\Delta \pi$ is osmotic pressure difference between the two solutions (') and (") separated by the membrane and $V_w$ and $V_f$ are the partial molar volume of the solvent and the filtrate volume, which is for a dilute solution is to a first approximation given by $\Delta n \approx V_w \equiv V_f$.

In electrodialysis change of the Gibb’s free energy for converting a feed solution into a concentrate and a diluate is given by:

$$
\Delta G_{\text{total}} = RT \left( n^c_s \ln \frac{C^c_s}{C^f_s} + n^d_s \ln \frac{C^d_s}{C^f_s} \right)
$$

(2.209)

Here $\Delta G$ refers to the Gibb's free energy change required for the production of the diluate, $C$ is the salt concentration, the superscripts f, c and d refer to the feed, the concentrate and the diluate, respectively.

2.5.2 Practical energy requirements in membrane processes

The minimum energy requirement for the separation of molecular mixtures, such salt solutions, discussed previously refers to an idealized, completely reversible process. In praxis such conditions never prevail and the energy requirements are usually significantly higher and rather different in different membrane separation processes. The apparatus does not represent an ideal machine in the thermodynamic sense. Since in membrane separation processes at least one component has to be transported through the membrane some energy will be needed to overcome the friction loss the component experiences while moving through the membrane matrix. This energy is dissipated as heat and thus is irreversibly lost. It depends very much on the system, i.e. on the membrane and its structure, and on the permeating components, and their interaction with the membrane material and the membrane process itself. The irreversible energy losses are directly proportional to the amount of material transported through the membrane and their friction with the membrane. Therefore, the irreversibly lost energy in microfiltration where pore flow with relatively little interaction with the membrane material dominates is much lower than in reverse osmosis where the transport is determined by a solution diffusion mechanism and the interaction of the permeating components with the membrane matrix is much higher.

2.5.2.1 Energy requirements in pressure driven processes

In pressure driven membrane processes such as micro- and ultrafiltration or reverse osmosis the total energy requirement for removing a certain amount of permeate from a feed mixture is than given by:
\[ E_{\text{tot}} = V_o \Delta p_{\text{appl}} \]  \hspace{1cm} (2.210)

Here is \( E_{\text{tot}} \) the total energy used in the process, \( V_o \) is the volume of the feed solution and \( \Delta p_{\text{appl}} \) is the applied hydrostatic pressure.

In reverse osmosis of seawater where a hydrostatic pressure between 30 and 40 bar is applied the total energy consumption is between 0.85 and 1.1 kWh for 1 m\(^3\) product water.

In microfiltration - and to a large extent also in ultrafiltration- where solutions with high molecular weight components or particles are treated the osmotic pressure is in general negligible low. The pressure loss due to friction with the membrane is also relatively low and thus the total energy consumption is low. Assuming a hydrostatic pressure of 2 bar, which is typical for micro- or ultrafiltration, the energy consumption is ca. 0.05 kWh to produce 1 m\(^3\) of filtrate.

2.5.2.2 Energy requirements in electrodialysis

In electrodialysis the process of producing a certain amount of product of a desired quality from a feed mixture is completely different than in reverse osmosis. To produce a certain amount of desalted product the ions are removed from the feed by transporting them under the driving force of an electrical potential difference through ion-exchange membranes. The reversible energy requirements for identical feed, product and concentrate solutions are the same in reverse osmosis and electrodialysis. The irreversible energy losses in electrodialysis are determined by the amount of ions that must be removed from the feed and their friction with the membrane and the water or other neutral components. This friction can be expressed by the electrical resistance of the membrane and the solutions, which again is proportional to the voltage drop. The total energy required in electrodialysis is thus given by:

\[ E_{\text{tot}} = I U \Delta t \]  \hspace{1cm} (2.211)

Here \( E_{\text{tot}} \) is the total energy used to produce a given amount of de-ionized water, \( I \) is the current flowing through an electrodialysis stack between anode and cathode, \( U \) is the voltage applied between the electrodes, and \( \Delta t \) the time need to achieve a certain degree of desalination. Under the assumption of ideal conditions, i.e. the current utilization is 100 %, the total energy required for the de-ionization of a given amount of feed solution is proportional to the flux of ions from the feed to the concentrate solution and given by:

\[ E_{\text{total}} = F V_d \left( C_s^c - C_s^f \right) U \]  \hspace{1cm} (2.212)
Here $F$ is the Faraday constant, $V$ the volume, $C$ is the concentration, $U$ is the applied voltage, the subscripts $s$ refer to cations or anions, respectively and the superscripts $c$ and $f$ refer to concentrate and feed, respectively.

The total electrical potential drop between the electrodes across an electrodialysis cell is only partly caused by the electrical resistance of the solutions and membranes, it is also due to the concentration potential established between the two solutions, determining the reversible part of the required energy. The electrical resistance results in an irreversible energy dissipation in the form of heat generation. Moreover, additional energy is also consumed by the electrode processes. In practical applications of electrodialysis the current utilization is less than 100% for several reasons. Firstly, ion-exchange membranes are not completely semipermeable and there is some transport of co-ions, secondly there is a substantial amount of water transport from the diluate to the concentrate due to osmotic and electroosmotic effects, and finally there is some current leakage through the manifold. An exact calculation of the energy requirement in electrodialysis is rather complex. It takes into account the electrical resistance of the diluate, the concentrate and the membranes, the concentration potentials between the solutions, and concentration polarization effects in the boundary layers at the membrane surface.

A comparison between the irreversible energy consumption in reverse osmosis and electrodialysis is illustrated in Figure 2.16 which shows the different principle of the two process.

The irreversible energy consumption in electrodialysis is directly proportional to the number of ions which are transferred from the feed to the concentrate solution. This is in contrast to reverse osmosis where the water has to permeate the membrane and the irreversible energy consumption is cause by the friction of the water with the membrane matrix. Thus in reverse osmosis is the irreversible energy consumption independent of the feed water concentration.
Fig 2.16 Schematic drawing illustrating the irreversible energy losses in reverse osmosis and electrodialysis due to friction losses of the permeating components within the membrane.

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### 3. Membrane preparation and characterization

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Summary
In this chapter different membrane preparation procedures are discussed. In the first part the preparation of porous membranes are described including techniques such as sintering of pressed powder, stretching of films extruded from polymers with partial crystallinity, or track-etching of polymer films. The most common technique of preparing porous membranes, i.e. the phase inversion process is discussed in more detail and the effect of the various preparation parameters on the final membrane structure is indicated. The polymers used today for the preparation of porous membranes are described.

Furthermore, the preparation of asymmetric and composite membranes is described. The two techniques used today for the preparation of asymmetric membranes, i.e. the diffusion induced phase separation process and the thermally induced phase separation process, are discussed in detail. Finally the preparation of special property membranes such as ion-exchange and liquid membranes with carrier enhanced transport properties are described.

In the second part of this chapter is devoted to membrane characterization. Membranes are characterized in terms of their structure, their transport properties, their electrical properties, and their chemical and thermal stability. The various techniques such as scanning electron microscopy, atomic force microscopy, bubble point measurement, liquid-liquid displacement, and flux and retention measurements are described and discussed.
3.1 General considerations
The most important part in any membrane separation process is the membrane itself. In the introduction of this outline membranes were described in terms of their structure and their function, and it was shown that membranes may be very different in terms of their structure, their transport properties, and their transport mechanism. Just as varied as the different membrane structures are the methods of making them. Some membranes are manufactured by simple sinter techniques of fine powders, others are prepared by irradiation and track etching of thin films or by inversion of homogeneous liquid mixtures or melts into heterogeneous solid phases. Composite membranes are prepared by dip-coating techniques, interfacial polymerization, and plasma polymerization. Inorganic membranes are prepared as composite structures using powder sintering techniques and the sol-gel method. Liquid membranes with mobile selective carriers are prepared as emulsions or supported in porous structures. Fixed carrier and ion-exchange membranes are prepared by introducing positively or negatively charged groups into suited polymer structures.

The selection of a suited base material and preparation technique depends on the application the membrane is to be used in. In some applications such as in gas separation or pervaporation the membrane material used as the barrier layer is of prime importance for the performance of the membrane. In other applications such as micro- or ultrafiltration the membrane material is not quite as important. Membrane preparation procedures are often developed empirically and described in the literature often as detailed recipes.

Closely related to the membrane preparation is their characterization. In addition to the determination of the membrane transport properties membranes are also characterized by various methods in terms of their morphology and mechanical, chemical and electrochemical properties. Which of the different membrane characterization techniques are used depends on the membrane type and its possible application.

3.2 Membrane preparation
The various membrane preparation techniques will be described beginning with symmetric porous media used in microfiltration. The preparation of integral and composite asymmetric membranes will be discussed. Finally, special property membrane such as ion-exchange and liquid membranes will be treated. The variety of membrane structures is illustrated in Figure 3.1 which shows scanning electron micrographs of structures of commercially available membranes.
3.2.1 Preparation of porous membranes

Porous membranes consist of a solid matrix with defined holes or pores which have diameters ranging from less than 2 nm to more than 20 µm. They can be made from various materials, such as ceramics, graphite, metal or metal oxides, and various polymers. Their structure may be symmetric, i.e., the pore diameters do not vary over the membrane cross section, or they can be asymmetrically structured, where the pore diameters increase from one side of the membrane to the other by a factor of 10 to 1,000. Porous membranes are used in microfiltration and ultrafiltration. They can be classified according to their different characteristics such as (1) type of material, i.e. ceramic or polymer, hydrophilic or hydrophobic, (2) structure, i.e. symmetric or asymmetric, or (3) pore size and pore size distribution. The pore size is used to make a distinction between micro- and ultrafiltration membranes. Microfiltration membranes normally
have pore diameters larger than 20 nm, while ultrafiltration membranes have typical pore diameters between 2 nm and 20 nm. The pore size and pore size distribution is used as a parameter to characterize microfiltration membranes. Ultrafiltration membranes are mainly characterized by a so-called molecular weight cut-off and the sharpness of the molecular weight cut-off. Besides the pore size, the surface and bulk porosity are of practical relevance. The preparation techniques of porous structures are summarized in Table I.

Table 3.1: Porous membranes, their preparation and application

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>membrane material</th>
<th>pore size (μm)</th>
<th>preparation process</th>
<th>application</th>
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<tr>
<td>Symmetric porous structures</td>
<td>ceramic, metal, polymer</td>
<td>0.1 - 20</td>
<td>pressing and sintering of powder</td>
<td>microfiltration, sterilization of fluids and gases</td>
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<tr>
<td>Symmetric porous structures</td>
<td>polymer of partial crystallinity</td>
<td>0.2 - 10</td>
<td>extruding and stretching of film</td>
<td>microfiltration, burn dressing, battery separator</td>
</tr>
<tr>
<td>Symmetric porous structures</td>
<td>polymer</td>
<td>0.05 – 5</td>
<td>irradiation and etching</td>
<td>microfiltration, Point-of-use filter</td>
</tr>
<tr>
<td>Symmetric porous structures</td>
<td>polymer, metal, ceramic, glass</td>
<td>0.5 - 20</td>
<td>templet leaching, photo litography</td>
<td>microfiltration</td>
</tr>
<tr>
<td>Symmetric porous structures</td>
<td>polymer</td>
<td>0.5 - 10</td>
<td>temperature induced phase inversion</td>
<td>microfiltration</td>
</tr>
<tr>
<td>Asymmetric porous structures</td>
<td>polymer</td>
<td>0.001 –0.01</td>
<td>diffusion induced phase inversion</td>
<td>ultrafiltration</td>
</tr>
</tbody>
</table>

Porous membranes can be made of different materials such as polymers, ceramics, metals or glasses. The membrane material determines the mechanical properties as well as the chemical and thermal stability of the membrane. But its hydrophilicity or hydrophobicity also effects its
performance in a practical application. Hydrophilic membrane are less susceptible to adsorption
of species like proteins, colloids, etc and consequently less sensitive to fouling. However, they
show general poor chemical and thermal stability. The methods used most widely today for
making porous membranes are sintering of powders, stretching of films, irradiation and etching
of films, and phase inversion techniques.

3.2.1.1 Symmetric porous sintered membranes.
Sintering is a rather simple technique to obtain porous structures from organic as well as from
inorganic materials. A powder consisting of certain size particles is pressed into a film or plate
and sintered just below the melting point of the material. The structure of a typical sintered
membrane is shown in the scanning electron micrograph of Figure 3.2. This photograph shows
the surface of a microporous membrane made by pressing and sintering a plate of fine
polytetrafluoroethylene powder. The process yields a microporous structure of relatively low
porosity in the range of 10 to 40 %, and a rather irregular pore structure with a very wide pore
size distribution.

![Scanning electron micrograph of a sintered membrane prepared from a poly-tetrafluoro-ethylene powder](image)

The material selection for the preparation of sintered membrane is determined mainly by the
required mechanical properties and the chemical and thermal stability of the material in the
application of the final membrane. Sintered membranes are made on a large scale from ceramic
materials, glass, graphite, and metal powders such as stainless steel and tungsten. The particle size of the powder is the main parameter determining the pore sizes of the final membrane, typically ranging from 0.2 to 20 µm. The lower limit of the pore diameter is determined by the particle size of the powder. Sintered membranes can be made in the form of discs, candles, or fine-bore tubes. They are used for the filtration of colloidal solutions and suspensions. This type of membrane is also marginally suitable for gas separation and widely used today for the separation of radioactive isotopes such as uranium isotopes.

3.2.1.2 Stretched membranes.
Another relatively simple procedure for preparing microporous membranes is the stretching of a homogeneous polymer film of partial crystallinity by an orientation, stretching, and annealing process. This technique is mainly employed with films of polyethylene or poly-tetrafluoroethylene, which have been extruded from a polymer powder at close to its melting point coupled with a very rapid draw-down. The crystallites in the semi-crystalline polymer are aligned in the direction of drawing. After annealing and cooling the extruded film is stretched perpendicular to the direction of drawing. This leads to a partial fracture of the film and relatively uniform pores with diameters of 0.2 to 20 µm are obtained. A typical stretched membrane prepared from poly-tetrafluoro-ethylene is shown in the scanning electron micrograph of Figure 3.3. These membranes, which have a very high porosity up to 90 % and a fairly regular pore size can be produced as flat sheets as well as tubes and capillaries. They are now widely used for microfiltration of acid and caustic solutions, organic solvents, and hot gases.
The stretched membrane made out of poly-tetrafluoro-ethylene is frequently used as water repellent textile. This membrane, because of its very high porosity, has a high permeability for gases and vapors, but it is, up to a certain hydrostatic pressure, completely impermeable to aqueous solutions because of the hydrophobic nature of the basic polymer. Thus, the membrane e.g. is repellent to rain water but permits water vapor generated by the body to permeate. More recently, this membrane has also been used in a process referred to as membrane distillation to remove ethanol from wine or beer to produce low alcohol products. The membranes have also found medical applications as burn dressings and artificial blood vessels.

3.2.1.3 Capillary pore membranes.
Microporous membranes with very uniform, nearly perfectly round cylindrical pores are obtained by a process generally referred to as track-etching. The membranes are made in a two step process. During the first step, a homogeneous 6 to 15 µm thick polymer film is exposed to collimated charged particles in a nuclear reactor. As particles pass through the film, they leave sensitized tracks where the chemical bonds in the polymer back-bone are damaged. In the second
step, the irradiated film is placed in an etching bath. In this bath, the damaged material along the tracks is preferentially etched forming uniform cylindrical pores. The entire process is schematically shown in Figure 3.4. The pore density of a track-etched membrane is determined by the residence time in the irradiator, while the pore diameter is controlled by the residence time in the etching bath. The minimum pore diameter of these membranes is approximately 0.01 µm. The maximum pore size that can be achieved in track-etched membranes is determined by the etching procedure. The polymer will not only be dissolved along the sensitized track left by the penetrating particle but also on both surfaces of the film. Thus, with exposure time in the etching medium the pore sizes increase while the thickness of the film is correspondingly reduced.

The scanning electron micrograph in Figure 2.5 shows a typical track-etched polycarbonate membrane. Capillary pore membranes are prepared today mainly from polycarbonate and polyester films. The advantage of these polymers is that they are commercially available in very uniform films of 10 to 15 µm thickness which is the maximum penetration depth of collimated particles obtained from a nuclear reactor which have an energy of about 0.8 to 1 MeV. Particles with higher energy, up to 10 MeV, may be obtained in an accelerator. They are used today to irradiate thicker polymer films, up to 50 µm thickness, or inorganic materials such as mica. However, these membranes are not yet available on a commercial basis.
Because of their narrow pore size distribution and low tendency to plug, capillary pore membranes made from polycarbonate and polyester have found application on a large scale in analytical chemistry and microbiological laboratories, and in medical diagnostic procedures. Capillary pore membranes are used on an industrial scale for the production of ultra pure water for the electronic industry. Here, they show certain advantages over other membrane products because of their short "rinse down" time and good long-term flux stability. Because of their surface filter characteristics, particles retained by the membranes can be further monitored by optical or scanning electron microscopy.

The membranes are also used in standard clinical tests for red blood cell deformability studies. Human red blood cells have a diameter of approximately 6 to 8 µm. The human body, however, contains capillaries of approximately 5 µm in diameter. To pass through these vessels the blood cells have to deform correspondingly. Healthy cells will do this readily but malignant cells will not. By filtering blood through a 5 µm capillary pore membrane certain blood deficiencies can be monitored.

3.2.1.4 Template leaching techniques
Aluminum membranes with linear pores are formed by a so-called anodic oxidation process in
the presence of an acid electrolyte followed by subsequent etching in a strong acid bath. Pores are formed perpendicular to the membrane surface and have a distinctive conical shape. This technique requires thin and high purity aluminum foils leading to membranes with rather low mechanical stability. In most of the applications these membranes need to be supported. The pore diameter varies from 0.02 - 0.2 µm, which is controlled by the voltage, the time of oxidation, and the type of acid used in the process. This process was originally developed by Anotec, Ltd..

Fig.3 6 Scanning electron micrograph of a microporous membrane prepared by anodic oxidation

A second technique to produce porous microfiltration membranes is the use of micro-lithography and reactive ion etching. A silicon waver is provided with a silicon nitride coating of approximately 1µm by means of chemical vapor deposition. On top of the silicon nitride layer a photosensitive lacquer is applied by spin-coating. The lacquer layer is subsequently exposed to a mask pattern of UV radiation using a suitable UV source. After exposure the lacquer layer is developed in a NaOH solution resulting in a print of the mask pattern in the lacquer layer. These perforations are extended into the silicon nitride by reactive ion-etching at low pressures. Now the separating layer is formed. These membranes have an extremely narrow pore size distribution and a very high flux. Pore diameters are typically between 0.5 and 10 µm.
Fig. 3.7 Scanning electron micrograph of a porous membrane prepared by photo-etching process

A modification of the photo-etching process is using X-ray lithography combined with galvanforming. The principle of the process is shown in Figure 3.8.
An absorber mask consisting of an X-ray transparent layer and a gold absorber pattern produced by electron beam lithography is placed on a layer of photo-resist polymer such as poly-methyl-methacrylate. The absorber mask is transferred to the polymer layer by irradiation with X-rays. The portion of the polymer layer exposed to the X-rays is degraded and can be removed by a development step. The result is a structure as shown in Figure 3.9. To obtain high penetration depth and extreme accuracy in the structure X-rays of high intensity and collimation are needed. By applying galvano-forming a replica of the original structure can be prepared as illustrated in Figure 3.10. The primary structure is placed on an electrically conductive base acting as cathode. By electro-deposition of metal such as nickel is precipitated between the insulating primary polymer structure which is then removed by a solvent.
Fig. 3.10  Schematic diagram illustrating the preparation of a metal structure by galvanofoming.

The metal replica can then be used to produce secondary structures as indicated by Figure 3.11. Figure 3.12 shows the scanning electron micrographs of a honeycomb structure prepared be X-ray lithography and the nickel replica prepared by galvano-forming. The process of X-ray lithography in combination with galvano-forming and micro injection is capable of producing porous structures with extreme accuracy and high porosity from a multitude of materials including metals.
Fig. 3.11 Schematic diagram illustrating the production of secondary structure by vacuum reaction injection molding using a metal mold prepared as a replica from a primary structure.
3.2.1.5 Symmetric microporous phase inversion membranes.
Most commercially available symmetric microporous membranes are prepared by the so-called phase inversion process in which a polymer is dissolved in an appropriate solvent and spread as a 20 to 200 µm thick film on a plate, a belt, or a fabric support. A precipitant such as water is added to this liquid film causing separation of the homogeneous polymer solution into two phases, i.e. a solid polymer rich and a liquid solvent rich phase. The precipitated polymer forms a
porous structure containing a network of more or less uniform pores. A microporous cellulosic membrane made by phase inversion is shown in the scanning electron micrograph of Figure 3.13

Fig.3.13 Scanning electron micrograph of the surface of a microporous cellulose nitrate membrane prepared from a homogeneous polymer solution by water vapor precipitation

Microporous phase inversion type membranes can be made from almost any polymer which is soluble in an appropriate solvent and can be precipitated in a non-solvent. By varying the polymer, the polymer concentration, the precipitation medium, and the precipitation temperature, microporous phase inversion membranes can be made with a very large variety of pore sizes, from less than 0.1 to more than 20 µm, and with varying chemical, thermal and mechanical properties. These membranes were originally prepared from cellulosic polymers by precipitation at room temperature in an atmosphere of approximately 100 % relative humidity. Lately, symmetric microporous membranes are also prepared from Nylon 66, Nomex, polysulfone, and poly-vinylidene-difluoride by precipitation of a cast polymer solution in water. The phase inversion process is today by far the most important technique for obtaining porous structures. The fundamentals of the process will be discussed in more detail later.

Polypropylene or polyethylene can also be used for the preparation of microporous membranes. However, since these polymers are not readily dissolved at room temperature, the preparation technique must be slightly varied. Polypropylene, e.g., is dissolved in an appropriate amine at elevated temperatures. A solution of 20 to 30 % polymer is spread at elevated temperature into a
film. The precipitation of the polymer, however, is not induced by the addition of a non-solvent but merely by cooling the solution to a point where a two phase system forms. The resulting open foam structure is shown in Figure 3.14.

![Fig. 3.14 Scanning electron micrograph of the surface of a microporous polypropylene membrane precipitated by thermal gelation from a hot homogeneous polymer solution](image)

The pore size depends on polymer concentration, solvent system, solution temperature, and cooling rate. This membrane preparation technique is usually referred to as thermal gelation. It can be applied to metal alloys and glasses as well as polymer solutions.

The symmetric, microporous polymer membranes made by phase inversion are widely used for separations on a laboratory and industrial scale. Typical applications range from the clarification of turbid solutions to the removal of bacteria or enzymes, the detection of pathological components, and the detoxification of blood in an artificial kidney. The separation mechanism is that of a typical depth filter which traps the particles somewhere within the structure. In addition to the simple "sieving" effect, microporous phase inversion membranes often show a high tendency of adsorption because of their extremely large internal surface. They are, therefore, particularly well suited when a complete removal of components, such as viruses or bacteria is desired. They are suited for immobilization of enzymes or even microorganisms to be used in modern biotechnology. They are also widely used for culturing of microorganisms in water quality control tests. In this test, the water is filtered through a membrane which retains all
microorganisms. The membrane is then placed on a nutrient pad in an incubator for 24 to 48 hours. During this time, the microorganisms grow into easily visible colonies. Grid marked membranes assist in counting the colony density, which is an indication of water quality.

3.2.1.6 Symmetric microporous phase inversion membranes from inorganic materials.
Microporous membranes can also be prepared by phase inversion from glass or metal alloys. The preparation procedure is relatively simple: two different types of glass are homogeneously mixed; then, one glass type is dissolved and a network with well defined pore sizes in the range of less than 1 nanometer to several nanometers of the undissolved material is obtained. Porous glass membranes can be made in various configurations, such as flat sheet, tubes, and hollow fibers, which are of particular importance because of their high surface area. Microporous metal membranes can be prepared from metal alloys such as Ni-Al-Cr by subsequent leaching of one component. These membranes have found their main application in gas separation processes. While the microporous metal membranes are mainly used for gas separation, microporous glass membranes have been used only on the laboratory scale for various applications, such as separation of liquid macromolecular mixtures, desalination of sea and brackish waters, ultrafiltration of wastewater, and in artificial kidneys for detoxification of blood streams.

3.2.2 Asymmetric Membranes

The most important membrane used today in separation processes is composed of a rather sophisticated asymmetric structure. In this membrane, the two basic properties required of any membrane, i.e. high transport rates for certain components and good mechanical strength, are physically separated. An asymmetric membrane consists of a very thin (0.1 to 1 µm) selective skin layer on a highly porous (100 to 200 µm) thick substructure, as indicated in the scanning electron micrographs of Figure 3.15, which shows the cross section of (a) a symmetric and (b) an asymmetric membrane. The very thin skin represents the actual membrane. It may consist of homogeneous polymer or may contain pores. Its separation characteristics are determined by the nature of the polymer and the pore size in the skin, while the mass transport rate is determined by the skin thickness, since the mass transport rate is inversely proportional to the thickness of the actual barrier layer. The porous sublayer serves only as a support for the thin and fragile skin and
has little effect on separation characteristics or the mass transfer rate of the membrane.
Asymmetric membranes are used primarily in pressure driven membrane processes such as
reverse osmosis, ultrafiltration, or gas separation, as it is here that the unique properties in terms
of high mass transfer rates and good mechanical stability can be best utilized.

![Scanning electron micrographs showing the cross-section of a symmetric microfiltration and b) an asymmetric ultrafiltration membrane.](image)

In addition to high filtration rates, asymmetric membranes are very resistant to fouling.
Conventional symmetric structures act as depth filters and retain particles within their internal
structure. These trapped particles plug the membrane and so the flux declines during use.
Asymmetric membranes are surface filters and retain all rejected materials at the surface where
they can be removed by shear forces applied by the feed solution moving parallel to the
membrane surface.

Two techniques are used to prepare asymmetric membranes: One technique utilizes the phase
inversion process and leads to a membrane where the skin and the substructure consist of the
same polymer. This membrane is referred to as integral asymmetric. In the second technique an
extremely thin polymer film is deposited on a preformed porous substructure leading to so-called
composite membranes.

3.2.2.1.1 Preparation of integral asymmetric membranes by phase inversion
The development of the first integral asymmetric membranes by phase inversion was a major
breakthrough in the development of ultrafiltration and reverse osmosis. These membranes were
made from cellulose acetate and yielded fluxes 10 to 100 times higher than symmetric structures
with comparable separation characteristics. Asymmetric phase inversion membranes can be
prepared from virtually all polymers that are soluble at a certain temperature in an appropriate solvent or solvent mixture and can be precipitated as a continuous solid phase by either changing the temperature or the composition of the system by the following general procedures:

1. Cooling of a homogeneous polymer solution which separates at a certain temperature; in two phases
2. Evaporation of a volatile solvent from a homogeneous polymer solution with two or more solvents of different dissolution capacity
3. Addition of a non-solvent or non-solvent mixture to a homogeneous solution

All three procedures result in the formation of two phases, i.e. a liquid phase forming the membrane pores and a solid phase forming the membrane structure, which may be either symmetric and porous or asymmetric with a more or less dense skin at one or both surfaces of a porous bulk phase. The only thermodynamic presumption for all three preparation procedures is that the change of the free energy of mixing of the polymer system under certain conditions of temperature and composition is positive; that is, the system must have a miscibility gap over a defined concentration and temperature range.

A phase separation that is the result of a temperature change is called temperature induced phase separation (TIPS) and a phase separation caused by the addition of a non-solvent or non-solvent mixture to a homogeneous solution is referred to diffusion induced phase separation (DIPS). In the practical membrane preparation combination and certain variations of the basic TIPS and DIPS processes are used to prepare membranes with tailor-made structures and properties.

The practical membrane preparation by the DIPS process

For the preparation of integral asymmetric membrane generally the diffusion induced phase separation process is applied. The process consists of the following consecutive steps:

1) A polymer is dissolved in an appropriate solvent to form a solution containing 10 to 30 weight % polymer.
2) The solution is cast into a film of the order of 100 to 500 µm thickness.
3) The film is quenched in a non-solvent typically water or an aqueous solution.

During the quenching process the homogeneous polymer solution separates into two phases: a polymer-rich solid phase, which forms the membrane structure, and a solvent-rich liquid phase,
which forms the liquid-filled membrane pores. Generally, the pores at the film surface, where precipitation occurs first and most rapidly, are much smaller than in the interior or the bottom side of the film. This leads to the asymmetric membrane structure.

There are different variations to this general preparation procedure described in the literature; e.g., sometimes an evaporation step is used to increase the polymer concentration in the surface of the cast polymer solution and an annealing step during which the precipitated polymer film is exposed for a certain time period to hot water of 70 to 80 °C is applied in the preparation procedure of making cellulose acetate membrane with high salt rejection.

The original recipes and subsequent modifications for preparing asymmetric membranes are deeply rooted in empiricism. Detailed descriptions of membrane preparation techniques are given in the literature. Only after extensive use of the scanning electron microscope, which provided the necessary structural information, was it possible to rationalize the various parameters for the actual membrane structure forming processes. It then became evident that symmetric and asymmetric porous structures can be prepared by the DIPS process from any polymer/solvent mixture which forms, under certain conditions of temperature and composition, a homogeneous solution and separates at a different composition into two phases, i.e. into a polymer-rich phase which forms the solid membrane structure and a polymer-lean phase that forms the liquid pores of the membrane. A further condition, however, is that both phases are continuous. If the liquid phase is discontinuous, a closed-cell foam structure will be obtained and if the solid phase discontinuous, a polymer powder will be obtained instead of a rigid structure.

The actual phase separation or phase inversion can not only be induced by the addition of non-solvent but also by the controlled evaporation of a volatile solvent from a three-component mixture of solvent/precipitant/polymer, causing precipitation as the system becomes enriched in precipitant. This technique was used by Zsigmondy and more recently by Kesting for the preparation of ultrafiltration and reverse osmosis membranes. Alternatively, precipitation of a simple two-component polymer-solvent casting solution can be brought about by imbibing precipitant from the vapor phase. This technique was the basis of the original microporous membranes and is still used commercially today by several companies.

*The practical membrane preparation by the TIPS process*
In the temperature induced phase separation, i.e. the (TIPS) process, the precipitation of a casting solution is achieved by cooling a polymer solution which forms a homogeneous solution only at elevated temperature, e.g., polypropylene dissolved in N,N-bis-(2-hydroxyethyl)tallow amine. The temperature induced phase separation process generally results in a symmetric porous structure. Under certain experimental conditions, especially when combined with the diffusion induced phase separation process, it can also result in asymmetric structures. The temperature induced phase separation is not only applicable to polymers which, because of their poor solubility, would otherwise be inaccessible to the phase inversion membrane preparation technique; it can also be used for making microporous membranes from glass mixtures and metal alloys in combination with a leaching procedure, as indicated earlier.

Detailed recipes given in the literature for the preparation of microporous structures from polymers, metals, or glasses seem superficially very different. But in all cases, the basic membrane formation mechanism is governed by similar thermodynamic and kinetic parameters, such as the chemical potentials and diffusivities of the individual components and Gibb’s free energy of mixing of the entire system. Identification of the various process parameters and thermodynamic description of the phase separation process is the key to understanding the membrane formation mechanism - a necessity for optimizing membrane properties and structures.

3.2.2.2 Phenomenological description of phase separation

Phase separation in a homogeneous polymer solution due to a temperature change, evaporation of solvent, and addition of non-solvent can be illustrated with the aid of the phase diagram of a mixture consisting of a polymer, one or more solvents and non-solvents at constant or different temperatures. It must, however, be realized that the phase diagram is the thermodynamic description of an equilibrium state. In the membrane formation process the phase separation is also determined by kinetic parameters, and thermodynamic equilibrium is generally not obtained on a macroscopic scale. The thermodynamic description of the phase separation is relatively easy. The quantitative description of the kinetics of the actual membrane structure forming process is significantly more difficult. However, just a very general thermodynamic description of polymer- solvent or polymer- solvent-non-solvent system provides valuable information concerning the membrane structures obtained by the inversion process.
The simplest procedure for obtaining a porous structure is by cooling down a two component polymer-solvent mixture, which at sufficiently high temperature forms a homogeneous solution for all compositions, but at a lower temperature shows a miscibility gap over a wide range of compositions. This is illustrated schematically in Figure 3.16, which shows a phase diagram of a two component mixture of a polymer and a solvent as a function of temperature. The points in the diagram indicated as solvent and polymer represent the pure components and points on the line solvent-polymer describe mixtures of these two components at a certain temperature. Above a certain temperature the polymer and solvent form a homogeneous solution at all compositions. At other temperatures the system is not stable at certain compositions and will separate into two phases. The region of composition and temperature in which the system does not form a homogeneous solution is referred to as the miscibility gap which is surrounded by the binodale curve. In the miscibility gap liquid-liquid de-mixing occurs. If the polymer is highly crystalline further liquid-solid de-mixing can take place resulting in a pure crystalline polymer in equilibrium with a liquid polymer solution. If a homogeneous polymer-solvent mixture of a certain composition at a temperature $T_1$, as indicated by point A in Figure 16, is cooled to the temperature $T_2$, as indicated by point B, it will separate into two different phases, the composition of which is indicated by the points $B'$ and $B''$. The point $B''$ represents the polymer-rich phase and the point $B'$ the solvent-rich, polymer-lean liquid phase. The lines $B'-B$ and $B''-B$ represent the ratio of the amounts of the two phases in the mixture; that is, the overall porosity of the obtained porous system. If the polymer concentration in the polymer rich phase has reached a certain value it viscosity is increased to such an extent that it can be considered as solid. Or if the polymer is highly crystalline the polymer rich phase will further change into pure crystallized polymer and a polymer saturated solution. The polymer rich phase forms the solid membrane structure and the polymer lean phase the liquid filled pores.
Fig.3.16 Schematic diagram showing the formation of a microporous system by thermal precipitation of a two-component mixture exhibiting a miscibility gap at certain conditions of temperature and composition.

Phase separation induced by the evaporation of a volatile solvent from a three-component polymer solution.
This process is based on a three-component mixture, i.e. a polymer, a volatile solvent and a third component, which by itself is a non-solvent for the polymer. This three-component mixture is completely miscible over a certain composition range but exhibits a miscibility gap over another composition range, as indicated in Figure 3.17, which represents an isothermal phase diagram of the three components. The corners of the triangle represent the pure components. Boundary lines between any two corners represent mixtures of two components, and any point within the triangle represents a mixture of all three components. Within a certain compositionally defined range of thermodynamic states, all three components are completely miscible, whereas in a different range - the miscibility gap - the system separates into two distinct phases. If the volatile solvent is completely evaporated from a homogeneous mixture of 10% polymer, 60% solvent and 30% non-solvent, as indicated by point A in Figure 3.17, the composition of the mixture will change from that represented by point A to that represented by point B. At point B, the system consists of only two components: polymer and non-solvent. Since this point is located...
within the miscibility gap, the system is separated into two phases: a polymer-rich phase, indicated by point B’ forming the rigid structure, and the phase B” forming the liquid filled pores of the membrane.

Phase separation induced by the addition of a non-solvent to a homogeneous polymer solution. This technique can again be rationalized with the aid of a three-component isothermal phase diagram shown schematically in Figure 18. This phase diagram of the three-component mixture exhibits a miscibility gap over a wide range of compositions. If a non-solvent is added to a homogeneous solution consisting of polymer and solvent, the composition of which is indicated by the point A on the solvent-polymer line, and, if the solvent is removed from the mixture at about the same rate as the non-solvent enters, the composition of the mixture will change following the line A-B. At point C, the composition of the system will reach the miscibility gap and two separate phases will begin to form: a polymer-rich phase represented by the upper boundary of the miscibility gap and a polymer-poor phase represented by the lower boundary of
the miscibility gap. At a certain composition of the three-component mixtures, the polymer concentration in the polymer-rich phase will be high enough to be considered as solid. This composition is represented by point D in Figure 3.18, referred to as the point of solidification.

Fig. 3.18 Schematic diagram illustrating the formation of a porous system by addition of a non-solvent to a homogeneous polymer solution in a three-component mixture exhibiting a miscibility gap at certain conditions of temperature and composition

At this point, the membrane structure is more or less determined. Further exchange of solvent and non-solvent will lead to the final composition of the membrane, the porosity of which is determined by point B. Point B represents a mixture of the solid polymer-rich phase and the liquid solvent-rich phase of compositions B' and B" respectively. The description of the formation of porous systems by means of the phase diagrams, as illustrated in Figures 3.16 to 3.18, is based on the assumption of thermodynamic equilibrium. It predicts under what conditions of temperature and composition a system will separate into two phases and the ratio of the two phases in the heterogeneous mixture, i.e. the overall porosity. However, no information is provided about the pore sizes, which are determined by the spatial distribution of the two phases. Equilibrium thermodynamics is not able to offer any explanation about structural
variations within the membrane cross section, that is, whether the membrane has a symmetric or asymmetric structure or a dense skin at the surface. These parameters are determined by kinetic effects, which depend on system properties such as the diffusivities of the various components in the mixture, the viscosity of the solution, and the chemical potential gradients which act as driving forces for diffusion of the various components in the mixture. Because these parameters change continuously during the phase separation, which constitutes the actual membrane formation process, no transient states of equilibrium will be achieved. Especially in polymer systems, frozen states will often be obtained which are far from equilibrium and which can be stable for long time periods. The chemical potential and diffusivities of the various components in the system, and their dependencies on such parameters as composition, temperature, viscosity, etc., are difficult to determine by independent experiments and, therefore, are not readily available. This makes a quantitative description of the membrane formation mechanism nearly impossible. A qualitative description, however, which allows rationalization of the membrane formation and correlation of the various preparation parameters with membrane structures and properties, is possible.

3.2.2.4 Thermodynamic description of phase separation of a two component mixture
The Gibb’s free energy of mixture, which consists of two components, is given by the sum of the partial free energies, i.e. the chemical potentials of the two components in the mixture. The Gibb’s free energy of a two component mixture is:

\[ G_m = X_1 \mu_1 + X_2 \mu_2 \] (3.1)

Here \( G_m \) is the Gibb’s free energy of a mixture per mole, \( X \) is the mole fraction and \( \mu \) the chemical potential.

The dependence of the Gibb’s free energy on the composition of the mixture is shown schematically in Figure 3.19.
The change of the Gibb’s free energy of mixing of a two component system is given by:

\[ \Delta G_m = X_1 \Delta \mu_1 + X_2 \Delta \mu_2 \]  

(3.2)

The chemical potential is given by:

\[ \mu_1 = \mu_1^0 + RT \ln X_1 \]  

(3.3)

thus is:

\[ \Delta \mu_1 = \mu_1 - \mu_1^0 = RT \ln X_1 \]  

(3.4)

The same relation is true for the chemical potential of the second component.

Introducing these relations in Equation 3.2 leads to:

\[ \Delta G_m = RT (X_1 \ln x_1 + X_2 \ln x_2) \]  

(3.5)

Since \( \ln x \) is always negative \( \Delta G_m \) is always negative, i.e. two components will mix spontaneously when the Gibb’s free energy of mixing is negative.

\[ \Delta G_m < 0 \]  

(3.6)

The Gibb’s free energy of mixing is also given by:

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

(3.7)

Here \( \Delta H_m \) and \( \Delta S_m \) are the enthalpy and the entropy of mixing.
For an ideal mixture the enthalpy of mixing is zero and the entropy of mixing is always positive, i.e.

\[ T\Delta S_m > 0 \]  

(3.8)

If two components are not miscible over a certain range of composition \( \Delta G_m \) will be positive over the area the system is not miscible, i.e. in the miscibility gap. This is, e.g. the case when the enthalpy of mixing has a high positive value. This is indicated in Figure 20, which shows the Gibb’s free energy of mixing as a function of composition in a system with a miscibility gap at a certain temperature.

Fig. 3.20  Gibb’s free energy of mixing as a function of composition in a system with a miscibility gap at a certain temperature, i.e. \( T_1 \).

For a mixture which is stable over a certain composition range the first derivative \( d\Delta G/dX < 0 \), i.e. it is negative until the miscibility gap, i.e. the binodal curve is reached and reaches a maximum when the spinodal curve is reached, i.e. the mixture will spontaneously separate in two phases. The two phases are characterize by the fact that \( d\Delta G/dX = 0 \). The second derivative \( d^2 \Delta G \) is \( > 0 \) for a stable mixture. It will be zero when the spinodal curve is reached and the mixture becomes unstable and decomposes spontaneously. This is illustrated in Figure 3.21
which shows the schematic drawing of the Gibb’s free energy of mixing and its first and second derivative as a function of the composition of a mixture which has a miscibility gap over a certain range of composition.

Fig. 3.21 Schematic drawing showing the Gibb’s free energy of mixing and its first and second derivative as a function of the composition of a mixture which has a miscibility gap over a certain range of composition.

3.2.2.4. Structures of asymmetric membranes obtained by phase inversion
There are basically three different structures of asymmetric membranes obtainable by phase inversion. These structures are shown in the scanning electron micrographs of Figure 3.22., which shows 4 typical structures made by a diffusion induced phase separation.
Fig. 3.22 Scanning electron micrographs of the cross-sections of symmetric and asymmetric membranes showing a typical a) symmetric structure b) asymmetric "finger" structure, c) asymmetric "sponge" structure with graded pore size distribution, and d) asymmetric "skin-type" structure with an uniform pore size distribution in the substructure.

The "finger" type structure shown in Figure 3.22 b) is often obtained in ultrafiltration membranes. It is composed of a thin skin on a highly porous substructure with pores penetrating the membrane perpendicular like fingers or tubes from the skin to the bottom site. The porous substructure has practically no hydrodynamic resistance compared to the selective skin. This is due to its high porosity and unidirectional pores. The "finger"-type membrane structure is mechanically relatively weak and may collapse under high hydrostatic pressures. It is, therefore,
mainly used in processes which are operated at relatively low hydrostatic pressures such as ultrafiltration or pervaporation. The sponge-type structure with a graded pore size distribution shown in Figure 3.22 c) is mechanically much stronger and can be exposed to significantly higher hydrostatic pressures than the "finger"-type structure without collapsing. However, the hydrodynamic resistance of the substructure may be significant compared to that in the skin. This type of membrane is mainly used in reverse osmosis or gas separation when relatively large hydrostatic pressures are required to obtain satisfactory fluxes. The sponge-type structure, with a uniform pore size distribution, has a lower hydrodynamic resistance and can in many cases be dried out without losing its useful separation properties. The loss of flux is generally observed when membranes having a sponge-type structure with a graded pore size distribution are dried. Asymmetric skin-type membranes with different pore structures can be made today from an entire variety of polymers as indicated before. Polymers, that are used today on a commercial basis to prepare membranes by the phase inversion process for various applications and processes, are listed in Table 3.1

Tab. 3.1 Polymers used in commercially membranes prepared by phase inversion and their applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>EP, MF, UF, RO</td>
</tr>
<tr>
<td>Cellulose esters (mixed)</td>
<td>MF</td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>UF</td>
</tr>
<tr>
<td>Polyamide (aromatic, aliphatic)</td>
<td>MF, UF, RO</td>
</tr>
<tr>
<td>Polycarbonate (track-etched)</td>
<td>MF</td>
</tr>
<tr>
<td>Polyester (track-etched)</td>
<td>MF</td>
</tr>
<tr>
<td>Polymide</td>
<td>UF, RO, GS</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>MF</td>
</tr>
<tr>
<td>Polyethersulfone</td>
<td>UF, MF, GS</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>UF, MF, GS</td>
</tr>
<tr>
<td>Sulfonated polysulfone</td>
<td>UF, RO, NF</td>
</tr>
<tr>
<td>Polyvinylidenefluoride</td>
<td>UF</td>
</tr>
<tr>
<td>Metaphenylene-diamine +trimesoyl chloride(i)</td>
<td>RO</td>
</tr>
<tr>
<td>Polyethlenenimine +isophthaloyl chloride (i)</td>
<td>RO</td>
</tr>
</tbody>
</table>
3.2.3 Preparation of homogeneous membranes

A homogeneous membrane is merely a dense film through which a mixture of chemical species is transported under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components in a solution is directly related to their transport rates within the membrane phase, which are determined mainly by their diffusivity and concentration in the membrane matrix. An important property of homogeneous membranes is that chemical species of similar size, and hence similar diffusivities, may be separated when their concentration, that is their solubility in the film, is different. The membrane phase itself may be solid or liquid. The mass transport in homogeneous membranes occurs strictly by diffusion; thus permeabilities are rather low. Homogeneous membranes need, therefore, to be as thin as possible.

3.2.3.1 Homogeneous polymer membranes

Although there are a number of homogeneous membranes made from inorganic materials, such as glass or certain metals, the technically more important structures are of polymeric origin. Modern polymer chemistry is highly proficient in tailoring polymers to specific aims in terms of mechanical or thermal stability and chemical compatibility. In general, mass transfer will be greater in amorphous polymers than in highly crystalline or cross-linked polymers. Thus, crystallization and orientation are to be avoided as much as possible when high permeabilities and transmembrane fluxes are desired. However, physical properties and, in particular, the mechanical strength of the polymer as well as its selectivity may then be adversely affected, and the final product will represent a compromise between necessary strength, selectivity and mass-transfer rates. The principal aim is to create as thin a barrier as possible, consistent with the required strength and absence of pinholes and defects. The two basic membrane configurations are flat sheet and hollow fibers. Flat sheets can be prepared by casting from solution, by extruding from a polymer melt or by blow and press molding. Hollow fibers are generally made by extrusion with central gas injection. Because of their high selectivity for different chemical components homogeneous membranes are used in various applications, which in general involve the separation of different low molecular weight components with identical or nearly identical molecular dimensions. The most important applications of homogeneous polymer membranes
are in gas separation, pervaporation, and reverse osmosis. For the separation of gases silicon rubber, because of its relatively high permeability, is the more widely used basic material. For reverse osmosis, cellulose esters and various polyamides serve as the barrier polymers. Most technically utilized homogeneous polymer membranes consist of a composite structure where a very thin homogeneous selective polymer film is supported by a thicker microporous structure which provides the required mechanical strength.

3.2.3.2 Homogeneous metal and glass membranes
There is only one type of homogeneous metal membrane of technical importance. This is the palladium, or palladium alloy membrane used for the separation and purification of hydrogen. The permeability of hydrogen in palladium, palladium alloys, and several other metals such as platinum, silver, iron, nickel, etc., is several orders of magnitude higher than of any other gas. The permeability of hydrogen in palladium alloy membranes is highly temperature dependent. The separation is, therefore, carried out at elevated temperature (~400 °C). The membranes generally consist of 10 to 50 µm thick metal foils. Because of their high selectivity, these membranes are used for production of high purity hydrogen (> 99.99% H₂). Although the process seems technically feasible, there are only very few commercial plants in operation. The same is true for the use of homogeneous silica glass membranes, the only other homogeneous inorganic material which shows any promise to be used as selective barrier especially for the separation of helium. Like metal membranes, glass membranes are operated at elevated temperature. Until today, however, no commercial industrial size plants are in operation. Homogeneous glass membranes also have a high selectivity for H⁺-ions, thus they are used as the selective barrier in pH-electrodes. Their preparation is described in some detail in the literature and shall not further be discussed in this chapter.

3.2.3.3 Liquid Membranes.
Liquid membranes have gained increasing significance in recent years. Especially in combination with facilitated and coupled transport which utilizes selective "carriers", as discussed in detail in the previous section of this outline, to transport certain components such as metal-ions selectively and at a relatively high rate across the liquid membrane interphase. Liquid membranes consist of a thin oil film separating two phases which are aqueous solutions or gas
mixtures. The material used for the liquid membrane should be completely immiscible with water and should have a very low vapor pressure to guarantee long term stability. It is a relatively easy to form a thin oil film between two aqueous or gas phases. It is difficult, however, to maintain and control this film and its properties during a mass separation process. In order to avoid a break-up of the film, some type of reinforcement is necessary to support such a weak membrane structure. Two different techniques are used today for the preparation of liquid membranes. In the first preparation technique, leading to so-called supported membranes, the pores of a microporous membrane are filled with the selective liquid barrier material as shown in Figure 3.23 a). In the second technique, the liquid membrane is stabilized as a thin oil film by a surfactant in an emulsion-type mixture, as illustrated in Figure 3.23 b). In the supported liquid membranes, the microporous structure provides the mechanical strength and the liquid-filled pores the selective separation barrier. Both types of membranes are used today on a pilot-plant scale for the selective removal of heavy metal-ions or certain organic solvents from industrial waste streams. They have also been used rather effectively for the separation of oxygen and nitrogen.

![Schematic drawing of a) supported and b) unsupported liquid membrane](image)

Fig.3.23 Schematic drawing of an a) supported and b) unsupported liquid membrane

3.2.3.3.1 Supported liquid membranes.

The preparation of supported liquid membranes is extremely simple, once certain requirements concerning the selective barrier and the microporous support material are fulfilled. The liquid membrane material should have a low viscosity and low vapor pressure, i.e., high boiling point and when used in aqueous solutions, a low water solubility. Otherwise, the useful lifetime of the
membrane is rather limited. The microporous substructure should have a high porosity, a pore size small enough to support the liquid membrane phase sufficiently under hydrostatic pressure, and the polymer of the substructure should be hydrophobic in nature as most liquid membranes used in contact with aqueous feed solutions. In practice, liquid membranes are prepared by soaking a hydrophobic microporous membrane, such as a Goretex® (Gore Corp.) or Cellgard® (Celanese Corp.) type stretched polytetrafluorethylene or polyethylene membrane, in the hydrophobic liquid. This may consist of a selective carrier such as certain oximes or tertiary or quaternary amines dissolved in kerosene. The disadvantage of supported membranes is their thickness which is determined by the thickness of the microporous support structure, which is in the range of 10 to 50 µm, and, therefore, about 100 times the thickness of the selective barrier of an asymmetric polymer membrane. Thus, the fluxes of supported liquid membranes can be low even when their permeabilities are high.

3.2.3.3.2 Unsupported liquid membranes.

The preparation of the unsupported liquid membrane is more complex, as indicated in Figure 3.24. Here, two immiscible phases, i.e. the hydrophobic oil-type membrane phase and a water phase, often referred to as stripping solution, are mixed to form an emulsion of water droplets in a continuous oil phase which is stabilized by addition of a surfactant. This emulsion is then added to the second aqueous phase, the feed solution with the first emulsion forming droplets in the second aqueous phase. The overall result is the separation of two aqueous phases by an oil phase forming the liquid membrane.
Fig. 3.24  Schematic diagram illustrating the preparation of an emulsion-type liquid membrane

Ideally, droplets form in this process, in which the aqueous phase is surrounded by a relatively thin hydrophobic phase, the membrane, which is surrounded by a second continuous aqueous phase. In reality, the hydrophobic membrane phase and the surrounding aqueous phases are more fractionated and the diffusion pathways become longer as a result. With another aqueous solution, the component to be eliminated is supplied to the original emulsion and passes through the membrane into the internal solution.

3.2.3.4 Ion-exchange membranes.

Ion-exchange membranes consist of highly swollen gels carrying fixed positive or negative charges. The properties and preparation procedures of ion-exchange membranes are closely related to those of ion-exchange resins. As with resins, there are many possible types with different polymer matrixes and different functional groups to confer ion-exchange properties on the product. Although there are a number of inorganic ion-exchange materials, most of them based on zeolites and bentonites, these materials are rather unimportant in ion-exchange membranes and will not be discussed further.

There are two different types of ion-exchange membranes: (1) cation-exchange membranes which contain negatively charged groups fixed to the polymer matrix, and (2) anion-exchange membranes which contain positively charged groups fixed to the polymer matrix.

In a cation-exchange membrane, the fixed anions are in electrical equilibrium with mobile cations in the interstices of the polymer, as indicated in Figure 3.25.
Fig. 3.25 Schematic diagram of a cation-exchange membrane showing the polymer matrix with the negative fixed charges, the positive counter-ions and the negative co-ions.

This figure shows schematically the matrix of a cation-exchange membrane with fixed anions and mobile cations, which are referred to as counter-ions. In contrast, the mobile anions, called co-ions, are more or less completely excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed ions. Due to the exclusion of the co-ions, a cation-exchange membrane permits transfer of cations only. Anion-exchange membranes carry positive charges fixed on the polymer matrix. Therefore, they exclude all cations and permeable to anions only. The most desired properties for ion-exchange membranes are:

1. High permselectivity - an ion-exchange membrane should be highly permeable for counter-ions, but should be impermeable to co-ions.
2. Low electrical resistance - the permeability of an ion-exchange membrane for the counter-ions under the driving force of an electrical potential gradient should be as high as possible.
3. Good mechanical and form stability - the membrane should be mechanically strong and should have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions.
4. High chemical stability - the membrane should be stable over a pH-range from 1 to 14 and in the presence of oxidizing agents are

It is often difficult to optimize the properties of ion-exchange membranes because the parameters determining the different properties often act contrary to one another. For instance, a high degree of crosslinking improves the mechanical strength of the membrane but also increases its electrical resistance. A high concentration of fixed ionic charges in the membrane matrix leads to a low electric resistance but, in general, causes a high degree of swelling combined with poor mechanical stability. The properties of ion-exchange membranes are determined by two parameters, namely, the basic polymer matrix and the type and concentration of the fixed ionic moiety. The basic polymer matrix determines to a large extent the mechanical, chemical, and thermal stability of the membrane. Very often the matrix of an ion-exchange membrane consists of hydrophobic polymers such as polystyrene, polyethylene or polysulfone. Although these basic polymers are insoluble in water and show a low degree of swelling, they may become water soluble by the introduction of the ionic moieties. Therefore, the polymer matrix of ion-exchange membranes is very often cross-linked. The degree of crosslinking then determines to a large extent the degree of swelling, and the chemical and thermal stability, but it also has a large effect on the electrical resistance and the permselectivity of the membrane. The type and the concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane, but they also have a significant effect on the mechanical properties of the membrane. The degree of swelling, especially, is effected by the concentration of the fixed charges. The following moieties are used as fixed charges in cation-exchange membranes:

\[-\text{SO}_3^-, \text{COO}^-, \text{PO}_3^{2-}, \text{HPO}_2^-, \text{AsO}_3^{2-}, \text{SeO}_3^-\].

In anion-exchange membranes fixed charges may be:

\[-\text{NH}_3^+, \text{RNH}_2^+, \text{R}_3\text{N}^+, =\text{R}_2\text{N}^+, \text{R}_3\text{P}^+, =\text{R}_2\text{S}^+.\]

These different ionic groups have significant effects on the selectivity and electrical resistance of
the ion-exchange membrane. The sulfonic acid group, e.g., $-\text{SO}_3^-$ is completely dissociated over nearly the entire pH-range, while the carboxylic acid group $-\text{COO}^-$, is virtually undissociated in the pH-range $< 3$. The quaternary ammonium group $-\text{R}_3\text{N}^+$ again is completely dissociated over the entire pH-range, while the primary ammonium group $-\text{NH}_3^+$ is only weakly dissociated. Accordingly, ion-exchange membranes are referred to as being weakly or strongly acidic or basic in character. Most commercially available ion-exchange membranes have $-\text{SO}_3^-$ or $-\text{COO}^-$ groups, and most anion-exchange membranes contain $-\text{R}_3\text{N}^+$ groups.

Commercial ion-exchange membranes can be divided, according to their structure and preparation procedure, into two major categories, either homogeneous or heterogeneous membranes. In general, heterogeneous ion-exchange membranes have relatively high electrical resistances. Homogeneous ion-exchange membranes have a more evenly distribution of fixed ions and often lower electrical resistances.

3.2.3.4.1 Preparation procedure of homogeneous ion-exchange membranes.

The methods of making homogeneous ion-exchange membranes can be summarized by three different basic procedures:

a) *Polymerization or polycondensation of monomers, of which at least one must contain a moiety that either is or can be made anionic or cationic.*

The first membranes made by this procedure were prepared from phenol by polycondensation with formaldehyde according to the following reaction scheme:
Phenol is treated with concentrated H\textsubscript{2}SO\textsubscript{4} at elevated temperatures which leads to the phenolsulfonic acid in para form. This acid is reacted with a solution of formaldehyde in water. The solution is then cast into a film which forms the membrane after cooling to room temperature. Excess monomer is removed by washing the film in water.

Most of today’s cation- or anion-exchange membranes are made by the polymerization of styrene and divinylbenzene and subsequent sulfonation or amination. The cation-exchange membrane is obtained by the following reaction scheme:

For the preparation of anion-exchange membranes positively charged groups are introduced into the polystyrene by chloromethylation and amination with triamine according to the following reaction scheme:
b) Introduction of anionic or cationic moieties into a preformed film

Starting with a film makes the membrane preparation rather easy. The starting material may be a film from a hydrophilic polymer such as cellophane or polyvinyl alcohol, or a film from a hydrophobic polymer such as polyethylene or polystyrene. Ion-exchange membranes made by sulfochlorination and amination of polyethylene sheets for instance, have low electrical resistance combined with high permselectivity and excellent mechanical strength. The reaction scheme for the preparation of these membranes is given below:

and
c) Introduction of anionic or cationic moieties into a polymer chain followed by dissolving the polymer and casting it into a film.

Membranes made by sulfonation of polyetherketon or chloromethylated and aminated polysulfone according to the following reaction scheme may be cast around screens or other reinforcing materials to improve their strength and dimensional stability:

The co-ion transport and the swelling behavior can be decreased by cross-linking. The cross-linkage is done during the membrane formation step as indicated in the reaction scheme. The anion-exchange membrane is obtained by incorporating the mono-quaternary salt of 4,4'-diazabicyclo-[2.2.2]-octane (DABCO), into a polysulfone matrix as indicated in the following reaction scheme:
The anion-exchange layers are prepared from a solution of chloromethylated polysulfone by adding DABCO. Both the cation- as well as the anion-exchange membrane have excellent chemical and mechanical stability and good electrochemical properties as the data in the following table indicate.

Table: 3.2 Electrochemical properties of the cation- and anion-selective membranes prepared by sulfonating polyetherketon and aminating polysulfone

<table>
<thead>
<tr>
<th></th>
<th>anion-exchange membrane</th>
<th>cation-exchange membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>ion-exchange capacity (meq·g⁻¹)</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>membrane thickness (µm)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>area resistance (Ωcm²)</td>
<td>1.05</td>
<td>1.31</td>
</tr>
<tr>
<td>permselectivity (%)</td>
<td>97.5</td>
<td>98.5</td>
</tr>
<tr>
<td>swelling (%)</td>
<td>8</td>
<td>12.5</td>
</tr>
</tbody>
</table>

3.2.3.4.2 Special property ion-exchange membranes
In the literature, there are numerous methods reported for the preparation of ion-exchange membranes with special properties, for instance, for use as battery separators, ion-selective
electrodes, or in the chlor-alkali process. Especially membranes for the chlor-alkali industry are of commercial significance. These membranes are based on polytetrafluoroethylene and carry sulfone groups in the bulk of the membrane phase and carboxy-groups on the surface as the charged moiety. They combine excellent chemical stability with high selectivity and low electric resistance. A membrane introduced by DuPont as Nafion® is prepared according to the following reaction scheme in a several-step procedure:

![Chemical reaction](image)

This intermediate is reacted with hexafluoropropylene oxide to produce a sulfonyl fluoride adduct.

![Chemical reaction](image)

By heating with sodium carbonate the sulfonyl-fluoride-vinylether is formed, which is then copolymerized with TFE.

![Chemical reaction](image)

The resulting copolymer is extruded as a film and finally the ionogenic moiety is converted to membranes which carry sulfone-groups as the charged moieties by reacting the −SO2F groups with sodium hydroxide. The lifetimes of membranes under the aggressive conditions of chlor-alkaline process are in the range of 3 years.
Other special property membranes are developed for the production of table salt, or to be used as ion-selective electrodes, and in diffusion, and Donnan dialysis. Significant effort has also been concentrated on the development of anion-exchange membranes with low fouling tendencies.

*Monovalent ion permselective membranes*

For the production of table salt by concentration of sea water monovalent cation selective membranes were prepared by forming a thin positively charged layer on the surface of a cation-exchange membrane. Monovalent anion permselective membranes with a thin highly cross-linked layer on the membrane surface have also been developed. By such means the selectivity of sulfate compared to the one of chloride can be reduced from about 0.5 to about 0.01 and of magnesium compared to sodium from about 1.2 to about 0.1.

*Anion-exchange membranes of high proton retention*

By means of traditional membranes, it is not possible to apply electrodialysis in the recovery of acid in order to reuse the acid because of high proton leakage through the anion-exchange membranes. In general, since protons permeate easily through an anion-exchange membrane, acids can not be concentrated to more than a certain level by electrodialysis with high efficiency. Recently developed membranes, however, exhibit low proton permeabilities and enable efficient acid concentration.

*Anti-fouling anion-exchange membranes*

The anion-exchange membrane is more sensitive to fouling. The permeability of commercial anion-exchange membranes is limited in practical electrodialytical separations to components having a molecular weight of less than 100 Da. A molecular weight of 350 Da is to be considered as a maximum for any component to be transport through regular commercial membranes. Fouling of anion-exchange membranes often occurs when the anion is still small enough to penetrate into the membrane structure, but its mobility is so poor that the membrane is virtually blocked. To overcome this problem membranes were developed which are characterized by a high permeability for large organic anions. In general, the permselectivity of these membranes is lower than that of regular membranes. A membrane which is less sensitive to traces of detergents is available today from Ionics. Another type of anti-fouling anion-exchange membrane is produced by Tokuyama Soda. The membrane is coated with a thin layer of cation-exchange groups causing electrostatic repulsion of organic molecules.
Bipolar membranes

Bipolar membranes have recently gained increasing attention as an efficient tool for the production of acids and bases from their corresponding salts by electrically enforced accelerated water dissociation. Bipolar membranes can be prepared by simply laminating conventional cation- and anion-exchange membranes back to back. Laminated bipolar membranes often exhibit unsatisfactory water splitting capability. But special surface treatment of commercial ion-exchange membranes and subsequent laminating may yield bipolar membranes with satisfactory properties. Single film bipolar membranes and multilayer bipolar membranes fulfil most of the practical needs.

3.2.4 Composite membranes

In processes such as reverse osmosis, gas separation and pervaporation, the actual mass separation is achieved by a solution-diffusion mechanism in a homogeneous polymer layer. Since the diffusion process in a homogeneous polymer matrix is relatively slow, these membranes should be as thin as possible, as indicated before. Therefore, an asymmetric membrane structure is mandatory for these processes. Unfortunately, many polymers with satisfactory selectivities and permeabilities for the various components in gas mixtures or liquid solutions are not well suited for the phase inversion membrane preparation process. This has led to the development of the so-called composite membranes. A typical composite membrane is shown schematically in Figure 3.26. It is composed of a 20 to 1000 nm thin dense polymer barrier layer formed over an approximately 50 to 100 µm thick microporous film. Composite membranes are prepared in a two step process: (1) manufacturing of the microporous support, and (2) deposition of the barrier layer on the surface of this microporous support layer.
Composite membranes have several advantages over the integral asymmetric structures. In an integral asymmetric membrane, the selective barrier layer and the microporous support always consist of the same polymer. In a composite membrane, different polymers may be - and in general are - used for the microporous support and the selective barrier layer. This means polymers which show the desired selectivity for a certain separation problem, but have poor mechanical strength or poor film-forming properties, and which are therefore not suited for preparation into integral asymmetric membranes, may well be utilized as the selective barrier in composite membranes. This expands the variety of available materials for the preparation of semipermeable membranes considerably.

3.2.4.1 Composite membrane preparation techniques
Making composite membranes involves two completely different tasks. One is the preparation of a suitable microporous support and the second is the preparation of the actual barrier layer and laminating it to the surface of the support structure. The performance of a composite membrane is not only determined by the properties of the selective barrier layer, but it is also significantly effected by properties of the microporous support.

3.2.4.1.1 Preparation and deposition of the selective barrier layer on the microporous support
The techniques used for the preparation of composite structures may be grouped into four general procedures:
(1) Casting of the barrier layer separately, e.g., on the surface of a water bath and then laminating it on the microporous support film.

(2) Coating of the microporous support film by a polymer, a reactive monomer or prepolymer solution followed by drying or curing with heat or radiation.

(3) Gas-phase deposition of the barrier layer on the microporous support film from a glow discharge plasma.

(4) Interfacial polymerization of reactive monomers on the surface of the microporous support film.

Casting an ultrathin film of cellulose acetate on a water surface and transferring the film on a microporous support was one of the earliest techniques used for preparing composite reverse osmosis membranes. The actual selective barrier was prepared by dissolving 2-10 percent cellulose diacetate in a solvent exhibiting a low water solubility such as cyclohexanone. Casting an ultrathin film from a dilute acetone solution on a glass plate and releasing the film from the plate after the evaporation of the acetone by immersion in water was another method of preparing ultrathin selective barriers. Although both preparation techniques lead to barrier layers less than 100 nm with correspondingly high flux rates, they are not well suited for large scale industrial production.

Coating a microporous support structure by dipping it into a polymer or prepolymer solution was also first developed for the preparation of reverse osmosis membranes. Here, a microporous membrane prepared from mixed cellulose esters was first coated by a protective layer of polyacrylic acid to prevent the solvent of the polymer solution of the barrier layer, which consisted of, for example, cellulose triacetate in chloroform, from dissolving the support structure. This technique was later improved by using a microporous sublayer, which had better overall mechanical and thermal stability, and which was insoluble in the solvent of the barrier layer polymer, such as an "open" polysulfone ultrafiltration membrane. Today, dip coating is applied mainly for the preparation of composite membranes to be used in gas separation and pervaporation. Particularly, polymers such as polydimethylsiloxane, which are available as soluble prepolymer and which can easily be crosslinked by a heat treatment procedure, thus becoming insoluble in most solvents, are suited for the preparation of this type of composite membrane. If the pore dimension in the support membrane is selected properly, the prepolymer is unable to penetrate the support, and a rather thin uniform barrier layer of 0.05 to 1 µm
thickness can easily be prepared. A typical composite membrane prepared by dip coating is shown in Figure 3.27. It is the scanning electron micrograph of an asymmetric polysulfone ultrafiltration membrane which was coated by a 1 wt % solution of polydimethylsiloxane in an appropriate solvent followed by thermal crosslinking.

Fig. 3.27 Scanning electron micrograph showing a composite membrane with polydimethylsiloxane as the selective layer deposited on a polysulfone support membrane

Gas phase deposition of the barrier layer on a dry microporous support membrane by plasma polymerization was also successfully used for the preparation of reverse osmosis membranes. Many organic compounds having adequate vapor pressure can be used to form a barrier layer on a microporous support. The plasma reactions are rather heterogeneous not only involving polymerization but depolymerization and modification of functional groups. Although reverse osmosis membranes with excellent desalination properties showing salt rejection in excess of 99 %, and fluxes of 1.2 m$^3$ m$^{-2}$ d$^{-1}$ when tested with seawater, have been prepared on a laboratory scale. However, large scale industrial production utilizing plasma polymerization for the preparation of composite membranes seems to be difficult.

Today, by far the most important technique for preparing composite membranes is the interfacial polymerization of reactive monomers on the surface of a microporous support film. The first membrane produced on a large scale with excellent reverse osmosis desalination properties was developed in the early seventies in the North Star Research Institute under the code name NS 100. The preparation procedure of this membrane, which exhibited water fluxes of about 1 m$^3$ m$^{-2}$ d$^{-1}$ and salt rejections in excess of 99 % when tested with seawater at 60 bar transmembrane pressure, was rather simple. A polysulfone support membrane was soaked in an aqueous solution
of 0.5 to 1% polyethyleneimine, which was reacted interfacially at the membrane surface with a 0.2 to 1% solution of toluene diisocyanate in hexane. A heat curing step at 110 °C leads to further crosslinking of the polyethyleneimine. The preparation of composite membranes based on piperazine and trimesoyl chloride is shown schematically in Figure 3.28.

Fig. 3.28 Schematic diagram showing the formation of a composite membrane by interfacial polymerization of piperazine with trimesoyl chloride

The process seems to involve two types of reactions. In a first step, the piperazine reacts rapidly at the interface with the trimesoyl chloride to form a polyamide surface skin while amine groups below this surface remain unreacted. In the second heat treatment step, internal crosslinking of the polyethyleneimine takes place. Thus, the final membrane has three distinct layers of increasing porosity: (1) the dense polyamide surface skin which acts as the actual selective barrier, (2) a thin crosslinked polyethyleneimine layer which extends into the pores of the support film, and (3) the actual polysulfone support membrane.

Although the NS-100 membrane showed significantly higher salt rejection capability and higher fluxes than most integral asymmetric reverse osmosis membranes, further improvements were achieved by using aromatic diamines and triacyl chloride as reactants. One of these membranes, the FT-30, produced by FilmTec Corporation from monomeric diamine reactants such as m-
phenylenediamine or piperazine interfacially polymerized with trimesoyl chloride shows not only excellent desalination properties but also highly improved stability towards oxidizing agents.

3.3 Membrane Characterization

3.3.1 Characterization of micro- and ultrafiltration Membranes
Micro- and ultrafiltration membranes are used to separate macro-molecular components or particles from a, mostly, aqueous solution. Their properties are related to their performance in a practical application. Membranes should combine high flux with good separation properties. Therefore, micro- and ultrafiltration membranes are characterized by fluxes and their capability of separating certain components from a mixture. The fluxes are measured usually with ultra-pure water under standard conditions of temperature and pressure. The separation properties of ultrafiltration membranes are given by the so-called molecular weight cut-off (MWCO) value. Microfiltration membranes are characterized by their pore size and their pore size distribution.

Other importance characteristics are the nature of the membrane material (whether it is hydrophilic or hydrophobic), the structure of the membrane and their mechanical, chemical and thermal stability.

3.3.1.1 The pure water flux of micro- and ultrafiltration membranes
A characteristic property of micro- and ultrafiltration membranes is their “pure water flux” or “pure water permeability”. The flux, \( J \), through a porous medium is proportional to the transmembrane pressure, \( \Delta P \), and inversely proportional to the solvent viscosity, \( \eta \), as expressed in Darcy’s law.

\[
J_v = \frac{L_p \Delta p}{\eta} \tag{3.9}
\]

Here \( J_v \) is the transmembrane flux, \( L_p \) is the solvent permeability, \( \eta \) is the solvent viscosity and \( \Delta p \) the applied pressure.

For the determination of the pure water flux it is very important to use a certain water quality. However, there is no standard method for the determination of the pure water flux and companies
use their own standards, which makes a reliable comparison of pure water fluxes rather difficult. Generally de-ionized or distilled water with a conductivity of > 5 µS cm⁻¹, which is treated by microfiltration to remove suspended materials is used as a test solution. The flux is determined at different applied pressures and plotted as a function of the pressure. From the slope of the plot the permeability, L_p, is obtained.

Prior to the flux measurements the membranes should be pressurized by filtration of pure water at a hydrostatic pressure that is at the upper limit of the recommended operating pressure for one to two hours to compress the membrane to a stable value that will not further deform when used at lower pressures. Possible preservatives, often present in membranes, must be eliminated by a washing procedure.

Some inorganic membranes, like Al₂O₃ based types, show an apparent internal pore clogging when de-ionized water is used in the pure water flux measurements. In these cases an electrolyte solution is used for determining the membrane flux, e.g. a NaCl- or KCl-solution.

Typical pure water fluxes of microfiltration membranes vary from 500 - 50,000 liters m⁻² h⁻¹ bar⁻¹, while pure water fluxes of ultrafiltration membranes vary from 50 - 800 liters m⁻² h⁻¹ bar⁻¹.

In practical applications fluxes are normally much lower and a steep flux decline is observed during the first period of operation. This flux decline is mainly determined by membrane fouling which is generally more pronounced for microfiltration than for ultrafiltration. More details regarding membrane fouling will be discussed later.

### 3.3.1.2 Microscopic techniques

A variety of microscopic techniques are used to study membrane structures, such as Scanning Electron Microscopy (SEM), Field Emission Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy. The advantage of these techniques is that direct visual information of the membrane morphology is obtained. The different microscopic techniques require different preparation methods and have different resolution. SEM, e.g. has a resolution of up to 5 nm and provides good information on the structures of micro- and ultrafiltration membranes including pore sizes and pore shapes. To reach a high resolution high electron-beam energy has to be applied, which can damage the membrane samples.

The pore sizes and pore shapes of ultrafiltration membranes can also be determined TEM which has a resolution of 0.4 - 0.5 nm or by FESEM which has a resolution of 0.6-0.7 nm. The TEM technique
requires a significantly more complex preparation procedure and is mainly applied to determine the surface porosity of ultrafiltration membranes (Fane et al. 1981).

FESEM can be operated at accelerating voltages as low as 1 - 4 kV and reach a resolution of 0.7 nm. Therefore, pores in ultrafiltration membranes can be visualize by FESEM (Kim et al. 1992).

Sample preparation for SEM and FESEM analysis is relatively easy compared to the sample preparation for TEM. To visualize the cross sections of a membrane, e.g. it is immersed in ethanol or a water/ethanol mixture prior to cooling in liquid nitrogen. The sample is then fractured providing a rather clean fracture. The samples is glued with a conductive glue to a sample holder and sputtered with a thin layer of gold. The sputtered layer should be thinner than the structure features of the membrane to be studied.

Nowadays, low vacuum SEM’s, i.e. so-called environmental SEM are available which makes it possible to scan at samples without a conductive coating. The resolution is not as high as for coated samples and the magnifications of ca. 7500.

Figures 3.1 to 3.7 shows typical pictures of membrane structures that can be obtained by SEM techniques.

Besides electron microscopy, atomic force microscopy (AFM) is also applied to study membrane surface structures. AFM has a resolution of ca. 1 nm. Sample preparation is fairly simple, since no conductive coating is required. Therefore, samples need not to be dried and exposed to vacuum.

An interesting modification of the ordinary AFM technique was recently developed (Kamusewitz et al. 1995). A small transmembrane nitrogen gas pressure of 0.1 -1.5 bar causing a gas flow through the membrane which caused the tip to be lifted from the surface when passing a pore entrance during the scanning mode. This technique is referred to as pneumatic scanning force microscopy (PSFM) A schematic representation of this method is given in Figure 3.29.

![AFM tip](image_url)  
**Figure 3.29:** Schematic representation of pneumatic scanning force microscopy (PSFM)
3.3.1.4 Membrane separation properties determined by filtration test

Both micro- and ultrafiltration are pressure driven membrane processes using porous membranes. The separation of various components is based on a sieving mechanism, i.e. particles or molecules which are larger in size than the pores of a membrane are retained by this membrane. A relation for the membrane retention as a function of the particle size and the pore size was defined by (Ferry 1936). Ferry has given a relation between the pore and the particle radius. If the particles are spherical and have a radius $r_s$ and the membrane pores are cylindrical with a radius $r_p$ the following relation can be applied to describe the membrane solute rejection:

$$R = \left[ 1 - \left( 1 - \frac{r_s}{r_p} \right)^2 \right]^2$$

(3.10)

For the radius of the molecule either the radius of gyration or the hydrodynamic (Stokes) radius can be used. The Ferry model is rather simplified, but gives a good approximation of the expected retention when particle and the membrane pore radii are known.

Retention and Molecular weight cut-off

To describe the retention of ultrafiltration membranes usually the Molecular Weight Cut-Off (MWCO) is used. The MWCO is defined differently by different companies. Originally it was defined by Amicon Corporation as the molecular weight of the globular molecule which is retained by the membrane in filtration test to more than 90%. The MWCO determination is very sensitive for the experimental conditions, i.e. the solutes and their concentration used in the test, the applied pressure, and the temperature. Therefore, a comparison of retention data given by different manufacturers is general problematic. As test conditions for determining the ultrafiltration membrane cut-off a transmembrane pressure of 100 kPa, a feed solution concentrations of 0.1 % and a test temperature of 25 °C is recommended. Furthermore, a maximum of agitation of the feed solution at the membrane surface is required to minimize concentration polarization effects and small amounts of solution should be filtered to assure a constant feed concentration.

The retention is generally expressed in % and defined by:
Here \( R \) is the retention or rejection of a membrane, \( C_f \) and \( C_p \) are the feed and the permeate concentration.

The retention of molecules having identical molecular weights may be rather different when their shape is different. Globular proteins e.g., are rejected easier than branched polysaccharides or flexible polymers (Porter 1979). Adsorption of the solute to the membrane surface, e.g., might result in high “apparent” retention values when the experiment is performed for a very short time periods. Accumulation of solutes at the membrane surface due to concentration polarization effect can also obscure the retention measurements and have to be when the true, i.e. intrinsic retention shall be determined. These effects can be more or less eliminated by using low transmembrane pressures, low feed concentrations, and a high degree of agitation.

Manufactures of ultrafiltration membranes generally make use of marker molecules, e.g. dextrans and proteins, for the determination of the MWCO value of their membranes.

In addition to the molecular weight cut-off of a membrane the sharpness of the cut-off is importance for the practical application. The sharpness of the cut-off of a membrane is determined by measuring the retention of the membrane for components of different molecular weight and plotting the retention versus the molecular weight of the retained components as shown in Figure 3.30. This figure shows the characteristic curves of a membrane with a sharp and a diffuse cut-off. The sharpness of the cut-off of a membrane depends mainly on pore size distribution of the membrane. For practical applications the cut-off of a membrane should be as sharp as possible.
The bacterial challenge test

Micro- and ultrafiltration membrane are often used in the food and pharmaceutical industry for sterilization of solution. It this application it is important that membranes retain undesired microorganisms as completely as possible, i.e. the retention for microorganisms should be close to 100%. Therefore, these membrane are exposed to a bacterial challenge test. In this test the membrane is challenged with a solution containing a minimum concentration of organisms such as Pseudomonas Diminuta per cm$^3$ of solution (Cheryan 1998). The data obtained in bacterial challenge tests are normally expressed in terms of the log reduction value (LRV) which is given by:

$$\text{LRV} = \log \left( \frac{\text{Concentration of bacteria in feed}}{\text{Concentration of bacteria in product}} \right)$$  \hspace{1cm} (3.12)

Because the bacterial challenge test is a destructive test and is therefore not suited as an on-line quality control test. For this application the non-destructive diffusion test and the bubble-point integrity test is generally applied.

3.3.1.5 Membrane properties determined by membrane pore size measurement

In addition to filtration tests micro and ultrafiltration membrane are characterized by determining their pore size and pore size distribution. A number of techniques such as liquid liquid displacement, mercury intrusion, permoporosimetry, thermoporosimetry, etc. are used for the determination of the membrane pore size and pore size distribution. One of the more simple method is the so-called bubble point test.

The bubble point test

The bubble-point test is a structure integrity test in which the largest pore or hole in a membrane is determined. The bubble-point method is based on the capillary effect of small pores due to surface tension forces. In equilibrium these forces are balanced with gravity of the liquid in the pore. The principle is shown in Figure 3.31.
This equilibrium between surface tension forces and gravity of the liquid in the pore can be expressed by the following equation:

$$2\pi r_p \sigma \cos \phi = r_p^2 \pi h \rho g$$  \hspace{1cm} (3.13)

Here $r_p$ is the pore radius, $\sigma$ is the surface tension of the liquid in contact with air, $\cos \phi$ is the contact angle between the liquid and the wall of the pore, $h$ is the height of the liquid column, $\rho$, is liquid density and $g$, the acceleration of gravity.

The term $h \rho g$ in Equation (3.13) can be replaced by the pressure, $p$. This results in the LaPlace equation which is given by:

$$r_p = \frac{2\sigma \cos \phi}{p}$$  \hspace{1cm} (3.14)

The bubble point method is a fairly simple technique where the pores of a membrane are filled with a liquid. From the bottom side of the membrane nitrogen gas or air is introduced with increasing pressure. At a certain pressure the gas will replace liquid in the largest pores permeating the membrane, and a bubble will rise from the membrane surface can be observed.

Equation 3.13 (LaPlace equation) gives a relation for the surface tension between the liquid and the
gas and the required pressure to open up pores of a certain size. In the Bubble-point test mostly water or iso-propanol are used, where the surface tension of water/air is approximately 3.5 times higher than for iso-propanol/air.

Other techniques to determine the pore size and pores size distribution of a porous membrane that are also based on the LaPlace equation, but cover different pores size ranges when the same pressure range is applied, are mercury porosimetry, gas-liquid displacement and liquid-liquid displacement.

The mercury porosimetry

In mercury porosimetry a dry membrane is exposed to a certain volume of liquid mercury. The pressure applied to the mercury is slowly increased, while simultaneously the amount of mercury forced into the porous structure is measured. The largest pores will be filled first and the required pressure for the mercury to penetrate the porous structure increases with decreasing pore size. The required pressure corresponds to a certain pore radius and the amount of mercury that disappears in the membrane corresponds to the total volume of these pores. The interfacial tension of mercury and air is very high. Therefore, relatively high pressures are required to fill small pores. In polymer membranes only pores having a radius in excess of 1 µm can be detected reliably by mercury porosimetry. Furthermore, this technique does not distinct between dead-end pores and interconnective pores.

Gas-liquid displacement

The gas-liquid displacement technique is identical to the Bubble-point method. The pores of the membrane are generally filled with an organic solvent which has a lower surface tension than water. The solvent is forced out of the membrane pores by nitrogen gas, which is introduced with increased in pressure. As the pressure increases the liquid will be replaced by nitrogen in the largest pores first and a convective gas flow through these pores will occur. The gas flow is measured as a function of the applied pressure. When all the pores are opened a linear relationship between pressure and gas flow is observed when the pressure is further increased. Figure 3.32 shows schematically typical gas fluxes obtained as a function of pressure with a dry and a liquid filled membrane.
Fig. 3.32 Schematic drawing illustrating the gas/liquid displacement measurement to determine the pore size and pore size distribution of microfiltration membranes.

The mean flow pore size is given by the point where the 50% “dry” flow curve crosses the “wet” flow curve. The maximum pore size is given by the point where a first flow through the liquid filled membrane is observed. The minimum pore size is given by the point where the fluxes of the dry and the liquid filled membrane become identical. The Laplace equation describes the relationship between the pore radius and the applied pressure. The pore size distribution of a Nucleopore, 0.2 µm membrane, determined by a commercial device referred to as Coulter Porometer is given in Figure 3.33. In this instrument Porofil® is used as the organic liquid. The surface tension of Porofil®/air is relatively low and sizes of pores with a radius between 20 nm and 100 µm can be measured and the pore size distribution and surface porosity can be calculated.
Fig 3.33   Illustrating the determination of the pore size distribution of a Nuclepore membrane having a nominal pore diameter according to the manufacturer of 0.2µm

**Liquid-Liquid displacement**

Liquid-liquid displacement differs from gas-liquid displacement in the displacing medium; the liquid inside the pores is displaced by a second liquid instead of a gas. The two liquids applied should be immiscible. A typical liquid pair used is water/iso-butanol. Both liquids are first saturated with each other before one of the liquids is used to fill the pores and the other liquid is applied as replacement liquid. The experimental set-up for the determination of pore sizes by liquid liquid displacement is shown in Figure 3.34. A slow increase in the replacement liquid pressure pushes the liquid out of the largest pores first. With increasing in pressure the liquid in the smaller pores will also be replaced. The pore size distribution can be calculated from a plot of the flux versus the applied pressure.

Whether iso-butanol or water is used as displacing liquid depends very much on the nature of the membrane material. Due to swelling phenomena different results might be obtained dependent on the liquid placed inside the pores.

![Schematic representation of a typical liquid-liquid displacement set-up](image)

Fig. 3.34   Schematic representation of a typical liquid-liquid displacement set-up

The relation between the pore radius and the pressure required to open pores of a certain size is
again described by the LaPlace equation. To determine the pore size distribution it is assumed that the pores are cylindrical and flux can be described by the Hagen-Poiseuille equation which is given by:

$$J = \frac{\pi n r_p^4 \Delta p}{8 \eta A_m \tau \Delta z}$$

(3.15)

Where, $J$ is the flux, $n$ is the number of pores with radius $r_p$, $\eta$ is the viscosity, $A_m$ is the membrane surface area, $\tau$ is the tortuosity factor, $\Delta z$ the membrane thickness and $\Delta p$ the transmembrane pressure.

When a membrane with a pores size distribution, $dn/dr_p$, is considered the total flux can be expressed by:

$$J_{tot} = \int_{r_{min}}^{r_{max}} dJ = \int_{r_{min}}^{r_{max}} \pi \Delta p dn r_p^4 dr$$

(3.16)

The integration is carried out from $r_p = r_{min}$, the minimum pore radius accessible for permeation, until $r_p = r_{max}$. Both integrands are a function of $\Delta p$. The pore size distribution can now be found by differentiating the flux, as expressed in equation (3.16) with respect to the transmembrane pressure, $\Delta p$ twice, applying Leibnitz’ theorem. Ultimately, the following expression for the pore size distribution is obtained:

$$\left( \frac{dn}{dr_p} \right)_{r_{min}} = -\frac{\eta \tau \Delta p^6}{16 \pi \sigma^5} \frac{d^2 J(\Delta p)}{d\Delta p^2}$$

(3.17)

The pore size distribution can now be calculated when the flux as a function of the transmembrane pressure is measured.

Like in gas-liquid displacement only active pores contributing to transport are taken into account. Pore diameters of approximately 5-100 nm can be analysed using liquid-liquid displacement. The advantage of liquid-liquid displacement over gas-liquid displacement is the lower interfacial tension between liquid pairs compared to a gas/liquid pair. Therefore, pores of the same size can be opened at much lower pressures in liquid-liquid displacement. Table 3.3 shows the pressures required to open pores of 10 nm for different displacement systems. A second advantage is that
membranes are characterized in a wetted state and therefore more approximating real operating conditions.

Tab. 3.3  Different porosimetry techniques and the influence of the interfacial tension on the pressure required to open pores of 10 nm

<table>
<thead>
<tr>
<th>Technique</th>
<th>System</th>
<th>Interfacial tension (mN/m)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury porosimetry (G-L)</td>
<td>Air/Mercury (Θ=141.3°)</td>
<td>480</td>
<td>749</td>
</tr>
<tr>
<td>Bubble-point (G-L)</td>
<td>Air/Water</td>
<td>72.3</td>
<td>145</td>
</tr>
<tr>
<td>Coulter porometry (G-L)</td>
<td>Air/Porofil®</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>Gas-liquid displacement (G-L)</td>
<td>Air/t-Butanol</td>
<td>20.7</td>
<td>41</td>
</tr>
<tr>
<td>Liquid-Liquid displacement (L-L)</td>
<td>Water/iso-Butanol</td>
<td>1.85</td>
<td>3.7</td>
</tr>
<tr>
<td>Liquid-Liquid displacement (L-L)</td>
<td>Water/iso-Butanol/Methanol</td>
<td>0.35</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Thermoporometry
Thermoporometry is based on the micro-calorimetric analysis of a solid-liquid transition. Water has a different freezing point in porous systems than in a macroscopic device. As the pore size decreases the freezing point of water will decrease. Freezing point depression can be measured by a sensitive Differential Scanning Calorimetry (DSC).

The Kelvin equation describes the relation between the pore radius, \( r_p \), of cylindrical and the depression of the melting point, \( T_m \).

\[
r_p = \frac{2\sigma V T_m}{\Delta H_f \Delta T}
\]

(3.18)

Where, \( \sigma \) is the interfacial tension of the solid/liquid interface, \( \Delta H_f \) is the molar enthalpy of fusion, which is ±6 KJ/mol for water, \( V \) is the molar volume of the solid and \( \Delta T \) is the degree of
super-cooling ($\Delta T = T - T_m$).

Brun et al. (1977) introduced corrections for possible adsorption layers. Because the theory is based on equilibrium thermodynamics it is important to scan at a slow as possible rate, preferably below 1 Kelvin per minute.

Thermoporometry is suited to characterize pores with diameters in the range of 2 - 50 nm. Membranes are analysed in a wet state and therefore drying can be avoided. From the cooling and heating curves information on the pore shape can be obtained. Disadvantages of thermoporometry are e.g. a pore size limit of 2 nm due to the validity of the Kelvin relation. The largest drawback of this technique is that mostly pores in the sub-layer and dead-end pores are evaluated rather than the transport determining active pores in the thin skin layer. Therefore, this technique is most accurately applied for very well defined and preferably symmetric porous structures.

*Permporometry*

Analogous to the principles in gas adsorption/desorption permporometry is a technique where pores are either filled by controlled condensation of a vapor phase or where filled pores are emptied by controlled evaporation of the liquid inside the pores. The relation between the relative vapor pressure and the pore radius is given by the Kelvin equation.

\[
\ln \left( \frac{p_v}{p_o} \right) = -\frac{\sigma V_m}{RT} \cos \phi \left( \frac{1}{r_{k1}} + \frac{1}{r_{k2}} \right) \tag{3.19}
\]

To be able to determine a pore size distribution curve gas transport through the open pores is measured upon changing the relative vapor pressure.

This process can be performed in two different modes,

1) measuring the gas flux, while closing the pores by condensing vapor or
2) measuring the gas flux, while evaporating liquid inside the pores.

The adsorption and desorption processes are often not ruled by the same curvature of the gas-liquid interface and can therefore lead to hysteresis phenomena.

Gas transport through the membrane can be obtained by applying a partial pressure difference across the membrane. There is no overall pressure gradient across the membrane and gas
transport is completely governed by diffusion. The relative vapor pressure at the feed side and the permeate side should always be equal.

In practice permporometry is carried out with a membrane placed in a cell, where at both sides of the membrane a gas containing a certain relative vapor pressure flows. At the feed side a mixture of oxygen and nitrogen, e.g. air, is applied and at the permeate side pure nitrogen is applied as carrier gas. In this way an oxygen concentration gradient across the membrane is created. The relative pressure of an organic vapor is always identical at both sides, while the absolute pressure at both sides equals 1 atm. The organic vapor should have a low affinity for the membrane material to avoid swelling phenomena. Often cyclohexane and sometimes ethanol is used, dependent on the nature of the membrane matrix. An experimental set-up for permporometry is schematically shown in Figure 3.35.

![Schematic representation of a permporometry set-up for hollow fiber membranes](image)

**Fig. 3.35** Schematic representation of a permporometry set-up for hollow fiber membranes

To determine the number of pores that open up at a certain relative vapor pressure the diffusive flux of oxygen from the feed side to the permeate side and of nitrogen form the permeate side to the feed side are measured. Because the absolute pressure is 1 atm. and the pore radii are in the range of 1 - 25 nm transport of oxygen and nitrogen will be completely determined by Knudsen diffusion. The fluxes are given by:

\[
J = \frac{n \pi r_p^2 D_A \Delta p}{A_m RT \tau \Delta z}
\]

\(3.20\)
with

\[ D_k = \frac{2}{3} r_p \sqrt[4]{\frac{8RT}{\pi MW}} \]  

(3.21)

Here, \( J \) is the flux, \( n \) is the number of pores, \( r_p \) is the pore radius, \( D_k \) is the Knudsen diffusion coefficient, \( \Delta p \) is the partial pressure difference across the membrane, \( A_m \) is the membrane surface area, \( R \) the gas constant, \( T \) the temperature, \( \tau \) the tortuosity factor, \( \Delta z \) the toplayer thickness, and \( MW \) the molecular weight of the gas diffusing through the pore.

With regard to the values used for the tortuosity and the membrane skinlayer thickness some assumptions have to be made. For the tortuosity a value of \( \tau = 1 \) is often used in the calculations and for the thickness of the membrane skinlayer a value of \( \Delta z = 0.2 \) µm is advised, based on experimental evidence. Knowing the pore radius, now the number of pores available for gas transport can be determined. During the desorption process the accumulated oxygen flux is measured as a function of the relative vapor pressure and subsequently as a function of the pore radius as indicated in Figure 3.35.

![Graphs showing the accumulated oxygen flux and its derivative as a function of pore radius.](image)

Fig. 3.36  The accumulated oxygen flux and the derivative of the accumulated oxygen flux as a function of the pore radius for a 15 nm (diameter) Nucleopore membrane

The t-layer can be obtained from the permporometry measurement by extrapolation of the measured accumulated gas flux as a function of the pore radius to a value equal to zero. When the relative vapor pressure is reduced to zero, no t-layer is present. Therefore, a further increase in oxygen flux can only be attributed to the removal of the t-layer. Figure 3.36 schematically shows the different steps in the desorption process, as well as the relationship between the Kelvin
radius $r_k$, the pore radius $r_p$ and the t-layer.

Fig. 3.36 Different stages during the permoporometry desorption process

Because a continuous monitoring of the gas flux is practically not possible the flux in certain intervals is measured. This gas flux is then related to the average pore radius limiting the interval. Therefore, a more correct representation of the pore size distribution would be the differential number of pores ($dn/dr$) or the differential gas flux ($dJ/dr$) as a function of the pore radius. Combining equation (3.20) and (3.21) the flux $J_i$ through the pores with radius $r_i$ can be expressed by:

$$J_i = \frac{2}{3} \sqrt{\frac{8\pi}{\text{MWRT}}} \Delta p \frac{A_{\text{m} \tau \Delta z}}{n_i r_i^3}$$

(3.22)

The total flux through the membrane can then be obtained from the summation of equation (3.22) over the entire distribution of the pore radii as expressed by the following Equation:

$$J = \sum_i J_i = \frac{2}{3} \sqrt{\frac{8\pi}{\text{MWRT}}} \frac{\Delta p}{A_{\text{m} \tau \Delta z}} \sum_i n_i r_i^3$$

(3.23)

The summation term of this equation can be described by a continuous function:

$$\sum_i n_i r_i^3 = \int_{r_{\text{min}}}^{\infty} \frac{dn}{dr} r^3 dr$$

(3.24)

Combination of Equations (3.23) and (3.24) and integrating leads to:

$$\frac{dJ(r_{\text{min}})}{dr_{\text{min}}} = -\frac{2}{3} \sqrt{\frac{8\pi}{\text{MWRT}}} \frac{\Delta p}{A_{\text{m} \tau \Delta z}} \left[ r^3 \left( \frac{dn}{dr} \right) \right]_{r=r_{\text{min}}}$$

(3.25)
\[
\frac{\left( \frac{dn}{dr} \right)_{r_{\min}}}{\left( \frac{dJ(r_{\min})}{dr_{\min}} \right)} = \frac{2}{3} \sqrt{\frac{MWRT}{8\pi}} \frac{A_m \tau \Delta z}{\Delta p r_{\min}^3} \tag{3.26}
\]

or

\[
\frac{\left( \frac{dn}{A_m dr} \right)_{r_{\min}}}{\left( \frac{dJ(r_{\min})}{dr_{\min}} \right)} = \frac{2}{3} \sqrt{\frac{MWRT}{8\pi}} \frac{\tau \Delta z}{\Delta p r_{\min}^3} \tag{3.27}
\]

It should be noted that the driving force for transport, \( \Delta p \), is dependent on the flux through the membrane; higher oxygen concentrations will be found at the permeate side when more pores are open and thus the flux is higher. Therefore, the partial pressure difference across the membrane at \( J(r_{\min}) \) should be used in the calculations using Equations (3.26) and (3.27).

Permporometry characterizes pores with diameters between 2 and \( \pm 40 \) nm. The membranes characterized are in the dry state and only active pores are analysed. The technique can be applied to flat sheet membranes as well as hollow fiber membranes.
4. Membrane module and basic process design

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Summary
In this chapter the different commercial advantages and limitations of the various module types are discussed and their major applications are indicated. The main requirements for a module design such as good control of concentration polarisation, high packing density, and low production costs are pointed out. Furthermore, the integration of the modules in a certain membrane modules used today in large scale industrial applications will be described. The technical membrane process and different modes of operation such as batch, feed-and-bleed, and continuous or multi-stage operation are described.
4.1. General considerations

To use a membrane in a given application it has to be installed in a proper device which is generally referred to as membrane module. Membrane modules must meet certain requirements as far as their production costs, their packing density, energy consumption, and especially the control of concentration polarization and membrane fouling is concerned. A large number of different module types are described in the literature. In laboratory application often a stirred cell is used in batch or feed and bleed operation mode.

However, on a large industrial scale mainly six basic types are used today. These modules are shown schematically in Figures 4.1 to 4.8. They are quite different in their design, their mode of operation, their production costs, and the energy requirements for pumping the feed solution through the module. A very important criteria is the control of concentration polarization and membrane fouling. In some modules such as the tubular, the plate-and-frame and the capillary type module concentration polarization and membrane fouling can effectively be controlled by the proper feed flow. Other modules such as the spiral-wound and the hollow fiber module are more sensitive for membrane fouling. There is not one module type that serves all membrane processes and applications. The different modules which are commercially available today are designed for a certain application and process in which they provide the technical and commercially best solution. The same is true for the process design and mode of operation. In certain applications batch and feed-and-bleed operation is used while in other applications continuous operation is more efficient.

4.2 Membrane modules

The commercially available modules even if they are of the same type such as the plate-and-frame module or the spiral-wound module can vary significantly in detail often tailor-made for a certain application. Here only the basic concept of the different module types will be discussed.

4.2.1 The cartridge membrane module

The pleated cartridge filter membrane module, which is shown in Figure 4.1, is used mainly in dead-end microfiltration. It consists of a pleated membrane cartridge installed in a pressurized housing. The feed solution enters the filter from the housing side and the product is collected in a
center tube which is sealed against the housing by an O-ring. Cartridge type filters are operated at relatively low hydrostatic pressures of 1 to 2 bars. Their useful life is limited due to plugging of the membrane pores by the retained solutes.

Fig. 4.1 Schematic drawing showing a cartridge filter unit

The useful life of a cartridge filter depends very much on the feed solution constituents and their concentration. It can be a couple of days up to several months. Cartridge filters are disposable items. If the membrane which has the typical characteristics of a depth filter is blocked by the retained particles it can generally not be cleaned and the original flux restored. The main application of cartridge filters is in sterile filtration of water, beverages, such as wine, beer or fruit juices, and pharmaceutical solutions. Furthermore, they are used for the filtration of surface water for industrial or household use to remove particles and suspended matters and to serve as pre-filters in reverse osmosis water desalination plants. An important application of cartridge filters is in the production of ultra pure water for the electronic industry where they are used as point-of-use filters to remove all traces of particles from the ultra pure water used to rinse electronic components. The actual cartridge is made by pleating a membrane sheet and potting the ends by an appropriate resin or hot-melt-glue. Since the process of pleating the membrane puts a considerable mechanical stress on the membrane only materials that are rather flexible and
have a certain mechanical strength are suited for the fabrication of cartridge filters. The cartridge filter module provides a relatively high surface area per unit volume and the production costs are also relatively low.

4.2.2 The plate-and-frame membrane module
Another module type used on an industrial scale for various membrane separation processes including ultrafiltration, reverse osmosis, and gas separation is the plate-and-frame module. Its design has its origin in the conventional filter press-concept. The membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two endplates and placed in a housing as indicated in the schematic diagram of Figures 4.2a and 4.2b.

Fig. 4.2a Schematic drawing illustrating the concept of a plate-and-frame membrane module

The feed solution is pressurized in the housing and forced across the surface of the membrane. The permeate leaves the module through the permeate channel to a permeate collection manifold which in circular devices is central tube as indicated in the Figure 4.2b. Often the device contains one or more baffles to extend the path-length of the feed solution in the device.
There are various types of plate-and-frame modules on the market which offer, however, only slight variations in their basic configuration. In many plate-and-frame membrane modules the membranes can easily be exchanged. This makes the module suitable for batch-type operations and multi-purpose applications using different membranes for different separation tasks. Plate-and-frame units are mainly used in small scale applications such as in the production of certain pharmaceuticals, bioproducts, or fine chemicals. The housings and other components of plate-and-frame modules to be used in the food and pharma industry are made from stainless steel so that they can easily be steam sterilized. These units, however, are quite expensive and the
exchange of the membranes is labor intensive. Therefore, the plate-and-frame module is quite expensive. There is, however, one exception and that is the electrodialysis stack. The electrodialysis stack resembles also a plate-and-frame unit where cation- and anion-exchange membranes are stacked in alternating series between two endplates. A typical sheet-flow electrodialysis stack is shown in Figure 4.2c.

**Fig. 4.2c** Arrangement of cation- and anion-exchange membranes in an electrodialysis stack

It is a device to hold an array of membranes between electrodes in such a way that the streams being processed are kept separated. A gaskets between the membranes forms the individual cells and also contains manifolds to distribute the process fluids in the different compartments. The distance between the membrane sheets is industrial-size electrodialysis stacks typically between 0.5 to 2 mm. In a practical electrodialysis system, 200 to 1,000 cation- and anion-exchange membranes are installed in parallel between to electrodes and a stack contains 200 to 1000 m² of membrane area. Thus the membrane area per unit volume is relatively high. The electrodialysis stack will be discussed in more detail later.

**4.2.3 The spiral-wound module**

A variation of the basic plate-and-frame concept is the spiral-wound module, which is widely used today in reverse osmosis, ultrafiltration, and gas separation. Its basic design is illustrated in Figure 4.3.
The feed flow channel spacer, the membrane, and the porous membrane support form an envelope which is rolled around a perforated central collection tube and inserted into an outer tubular pressure shell. The feed solution passes in axial direction through the feed channel across the membrane surface. The filtrate is moved along the permeate channel and is collected in a perforated tube in the center of the roll. Small spiral wound units consist of just one envelope which limits the total membrane area that can be installed in one unit to about 1 to 2 m$^2$. The main reason for the limitation of the surface area which can be installed in a module containing one single envelope is the pressure drop encountered by the permeate moving down the permeate channel to the central collection tube. Because the channel in a practical unit is very narrow its length is limited to 2 to 5 m. A significantly longer path would result in an unacceptable pressure drop in the permeate channel. To install larger membrane surfaces in a spiral wound module a multi-leaf arrangement is used as indicated in the Figure 4.3b.
Commercial spiral wound modules are about 1 meter long and have a diameter of 10 to 60 cm. The membrane area in a spiral-wound element is 3 and 60 m². Generally, 2 to 6 elements are placed in series in a pressure vessel.

The spiral-wound module provides a relatively large membrane area per unit volume. The large scale production is quite cost effective and module costs per membrane area are quite low. The major application of the spiral-wound module is in reverse osmosis sea and brackish water deslination. But it is also extensively used in ultrafiltration and gas separation. However, the spiral-wound module is quite sensitive to fouling, and the feed channels can easily be blocked and particles or fibers should be removed from the feed solution by a proper pretreatment procedure.

4.2.4 The tubular membrane module

Fig. 4.3b Schematic drawing illustrating the construction of a multi-leaf spiral-wound module
While the previously described three membrane module types required flat sheet membrane material for their preparation, special membrane configurations are needed for the preparation of the tubular, capillary, and hollow fiber modules.

The tubular membrane module consists of membrane tubes placed into porous stainless steel or fiber glass reinforced plastic pipes. The pressurized feed solution flows down the tube bore and the permeate is collected on the outer side of the porous support pipe, as indicated in Figure 4.4. The diameters of tubular membranes are typically between 1-2.5 cm. In some modules, the membranes are cast directly on the porous pipes and in others they are prepared separately as tubes and then installed into the support pipes. Today, tubular modules are used in ultrafiltration at low hydrostatic pressures. This allows the membrane tubes to be made by a welding or gluing procedure of flat sheet membranes that are cast on a relatively thick and mechanically strong porous polyester support material. These tubes which have a diameter of 0.5 to 1 cm do not need additional support when operated at hydrostatic pressures of less than 2 to 4 bars.

Usually, 10 to 30 individual tubes are installed in a larger tube and potted at the end of the tube. The feed solution is fed in parallel through the tubular bundle while the permeate of the individual tubes is collected in the outer shell tube as indicated in the schematic drawing of Figure 4.4b. The main advantage of the tubular module is that concentration polarization effects and membrane fouling can be easily controlled, and plugging of the membrane module is avoided even with feed solutions that have very high concentration of solid matter and thus high viscosity. The disadvantage of the tubular module design is the low surface area, that can be installed in a given unit volume, and the very high costs. Therefore, tubular membrane modules are generally only applied in applications where feed solutions with high solid content, and high viscosity have to be treated and other module concepts fail due to membrane fouling and module plugging. This is the case in certain applications in the food and pharma industry and in the treatment of certain industrial effluents.
4.2.5 The capillary membrane module

The capillary membrane module, which is shown schematically in Fig. 4.5, consists of a large number of membrane capillaries with an inner diameter of 0.2 to 3 mm arranged in parallel as a...
bundle in a shell tube. The feed solution is passed down the center of the membrane capillary and the filtrate, which permeates the capillary wall, is collected in the shell tube.

Fig. 4.5. Schematic diagram showing a capillary membrane module

The capillary membrane module requires membranes in a self-supporting capillary configuration, which when asymmetrically structured, carry the selective barrier on the inner side of the capillary, as indicated in the scanning electron micrograph of Figure 4.6, which shows a typical capillary, ultrafiltration membrane prepared in a wet-spinning process.

Fig. 4.6 SEM of a capillary membrane with the selective „skin“ on the inside of a capillary

The capillary membrane module provides a high membrane area per module volume. The production costs are very low and concentration polarization and membrane fouling can
effectively be controlled by the proper feed flow and back-flushing of the permeate in certain time intervals. The main disadvantage of the capillary membrane module is the required low operating pressure. Because of the limited stability of the capillary membranes operating pressures generally can not exceed 4 to 6 bars. Therefore, the capillary membrane is used in applications where low transmembrane pressures are applied, i.e. in dialysis, microfiltration, and low pressure ultrafiltration. The most significant application of the capillary membrane module is as artificial kidney.

4.2.6 The hollow fiber membrane module
The same basic spinning process is used for the preparation of hollow fiber membranes, which have an outer diameter of 50 to 100 µm. In hollow fiber membranes, the selective layer is on the outside of the fibers, which are installed as a bundle of several thousand fibers in a half loop with the free ends potted with an epoxy resin in a pressure tube as indicated in Figure 4.7. The filtrate passes through the fiber walls and flows up the bore to the open end of the fibers at the epoxy head.

![Schematic drawing illustrating the construction of a hollow fiber module](image)

Fig. 4.7 Schematic drawing illustrating the construction of a hollow fiber module
The hollow fiber membrane module has the highest packing density of all module types available on the market today. Its production is very cost effective and hollow fiber membrane modules can be operated at pressures in excess of 100 bars. The main disadvantage of the hollow fiber membrane module is the difficult control of concentration polarization and membrane fouling. When operated with liquid solutions the modules do not tolerate any particlals, macromolecules or other materials that may easily precipitated at the membrane surface. Therefore, an extensive pretreatment is required when hollow fiber membranes are used for the treatment of liquid mixtures. The main application of the hollow fiber module is today in reverse osmosis desalination of sea water and in gas separation. Both application require high operating pressures and low cost membranes which have a long useful life. In reverse osmosis, of sea water an extensive pretreatment of the sea water is required.

4.2.7 Other membrane modules

There are several more membrane module concepts, such as the rotating disk module or the transversal flow module. In a rotating disk module the membranes are arranged as in the circular plate-and-frame module. However, the feed solution is not pumped through the module but the membrane plates are rotating and thus providing some turbulence in the feed solution at the membrane surface. This module is rather costly per installed membrane area and is used only in very specific applications in the pharmaceutical industry when solutions with very shear sensitive constituents have to be processed.

The transversal flow capillary module which is shown in Figure 4.8 is used mainly in dialysis operations. It provides good control of concentration polarization at relatively low flow velocities also on the out-side of the capillaries which are arranged perpendicular to the feed flow. Therefore, high turbulence can be obtained at relatively low flow velocities. The transversal flow module provides a relatively large membrane area per unit volume and production costs are also quite low.
Fig. 4.8  Schematic diagram illustrating the concept of the transversal flow membrane module

In the following table the different the more significant membrane modules, there costs per membrane area, and main application are summarized.
Tab. 4.1 Commercially available membrane modules, their costs and major applications

<table>
<thead>
<tr>
<th>Membrane module</th>
<th>Membrane area per unit volume (m² m⁻³)</th>
<th>Membrane costs</th>
<th>Control of concentration polarization</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter cartridge module</td>
<td>800 - 1000</td>
<td>low</td>
<td>Very poor</td>
<td>Dead-end MF</td>
</tr>
<tr>
<td>Plate-and-frame module</td>
<td>400 - 800</td>
<td>medium</td>
<td>good</td>
<td>MF, UF, RO, D, ED</td>
</tr>
<tr>
<td>Spiral-wound module</td>
<td>800 - 1200</td>
<td>low</td>
<td>good</td>
<td>UF, RO, GS</td>
</tr>
<tr>
<td>Tubular module</td>
<td>20 - 100</td>
<td>very high</td>
<td>very good</td>
<td>MF, UF, RO</td>
</tr>
<tr>
<td>Capillary module</td>
<td>600 - 1200</td>
<td>low</td>
<td>very good</td>
<td>UF, MF, D, SLM</td>
</tr>
<tr>
<td>Hollow fiber module</td>
<td>2000 - 5000</td>
<td>very low</td>
<td>very poor</td>
<td>RO, GS</td>
</tr>
</tbody>
</table>

MF = microfiltration
UF = ultrafiltration
RO = reverse osmosis
D = dialysis
ED = electrodialysis
GS = gas separation
5. Concentration polarization and membrane fouling

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Summary
In this chapter the causes and consequences of concentration polarization and membrane fouling are discussed. The causes for concentration polarization are identical in all membrane separation processes. The consequences are quite different in the different processes. However, in all membrane process concentration polarization and membrane fouling is effecting the efficiency of the separation process. In the first part of this chapter concentration polarization phenomena in pressure driven membrane processes will be described and the various process parameters such as membrane module design feed flow velocities, feed composition, etc. will be discussed. Then the consequences of concentration polarization such as the increase of the osmotic pressure of the feed solution or the precipitation of certain feed solution constituents at the membrane surface will be treated and the various mathematical models used to describe concentration polarization phenomena are discussed. Then concentration polarization effects and its consequences in other membrane processes such as electrodialysis, dialysis and pervaporation will be described. Finally membrane fouling, its causes consequences and procedures for its prevention are described.
5.1 General considerations

Even if for a certain mass separation task the proper membrane is available there are various engineering aspects to be considered that can affect the economics of the process considerably, or even make it technically impossible. A major problem in all membrane separation processes is the decline of the transmembrane flux due to concentration polarization effects and the formation of cake or gel layers by feed solution constituents retained by the membrane. Equally devastating for the performance of a process is membrane fouling. Membrane fouling is a more general term it may be the result of concentration polarisation it may also be the consequence of adsorption of feed solution constituents at the membrane surface and especially in microfiltration also within the membrane structure. The control of concentration polarization and membrane fouling is a major problem in the design of membrane separation processes and equipment.

Concentration polarization effects will occur in all separation processes. Its consequences, however, are especially severe in membrane processes. When in a mass separation procedure a molecular mixture is brought to a membrane surface, some components will permeate the membrane under a given driving force while others are retained. This leads to an accumulation of retained material and to a depletion of the permeating components in the boundary layers adjacent to the membrane surface. This phenomenon is referred to as concentration polarization. The causes and consequences of concentration polarization may be rather different in different membrane processes. Often the adverse effects of concentration polarization are intensified by an adsorption of certain feed mixture constituents at the membrane surface. This phenomenon is referred to as membrane fouling. It is often observed when solutions containing biological materials such as proteins have to be processed but also inorganic materials especially polyelectrolytes can cause severe fouling effects. A special form of membrane fouling is the so-called biofouling. In this case micro organisms are accumulated and attached at the membrane surface. The actual mechanism of biofouling is rather complex and involves the formation of a so-called conditioning film which consist of organic polymeric material which than leaves the membrane surface within the biocompatible range for attachment of film-forming bacteria. Biofouling is especially severe in reverse osmosis of sea water and its control is crucial for the reliable operation of reverse osmosis desalination plants. While concentration polarization it can be minimized by hydrodynamic means such as the feed flow velocity and the membrane module design is the control of membrane fouling more difficult. Membrane fouling is influenced by
chemical nature of the membrane material and the feed solution constituents and in addition by fluid dynamic measures extensive feed water pre treatment as well as the dosage of special chemicals may be required. The causes and consequences of concentration polarization and membrane fouling as well as necessary means to control it depends on the feed water composition and on the membrane process.

5.2 Concentration polarization and membrane fouling in pressure driven membrane processes

The causes and consequences of concentration polarization in pressure driven membrane processes, such as reverse osmosis, ultra- and microfiltration have been studied extensively. While the causes for concentration polarization are identical in all three processes the consequences are rather different. When water selectively permeates a reverse osmosis or ultra- and microfiltration membrane, the retained solutes are accumulated at the membrane solution interface. Thus a concentration gradient between the solution at the membrane surface and the bulk is established which leads to a back transport of the material accumulated at the membrane by diffusion and eventually other means. This phenomenon is referred to as concentration polarization. In reverse osmosis mainly low molecular weight materials are separated from a solvent such as water. The feed solutions often have a considerable osmotic pressure. For example sea water has an osmotic pressure of ca. 24 bar. In reverse osmosis concentration polarization leads to an increase in the osmotic pressure which is directly proportion to the solute concentration at the membrane surface and thus a decrease in the transmembrane flux at constant applied hydrostatic pressure. Furthermore, the quality of the filtrate is impaired since the solute leakage through the membrane is also directly proportional to the solute concentration at membrane feed side surface.

In ultra- and microfiltration only macromolecules and particles are retained by the membrane. The osmotic pressure of the feed solution is generally not as high as in solutions treated by reverse osmosis. However, the applied hydrostatic pressure are generally quite low, too and under certain conditions also especially in ultrafiltration increased osmotic pressure due to concentration polarization effecting the trans-membrane flux. More important in ultra- and microfiltration is the fact that the diffusive back transport of the components retained be the membrane into the bulk of the feed solution is due to their high molecular weight rather slow and often the solubility of the retained material is exceeded and precipitation will occur at the
membrane surface forming a more or less dense solid layer. This layer, which often exhibits membrane properties itself, can effect the membrane separation characteristics significantly by reducing the transmembrane flux and changing the rejection of lower molecular weight components. This is especially problematic when different molecular weight materials are to be fractionated.

To describe the concentration polarization in membrane filtration processes mathematically a relationship is needed, which relates the solute concentration at the membrane surface to that in the bulk and permeate solution, the transmembrane flux, and the fluid flow conditions in the boundary layer between membrane surface and bulk solution. There are two basic approaches to treat this problem:

1. The application of the so-called film model with the appropriate mass transfer coefficients to described the solute transport into and out of the boundary layer;
2. The solution of the transport equations for the fluid velocity field to obtain an expression for the local concentration at any point in the feed solution.

The second approach is more rigorous but often difficult to apply. When the concentration polarization does not lead to a precipitation of solutes at the membrane surface can its causes and consequences relative well described as a function of the various hydrodynamic parameters and membrane and feed solution properties by simple mathematical models. Significantly more complex is a treatment when the concentration polarization leads to a precipitation of the solutes. Here very often time dependent effects such as a densification a formed gel or cake layer will influence the membrane flux as well as its separation characteristics.

5.2.1 Concentration polarization without solute precipitation

The mass transport at the membrane surface in filtration processes can be calculated the material and momentum balance by a numerical integration of the transport equations for fluid and solutes. The numerical solution of these equations is rather complex even after introducing certain simplifications such as complete solute rejection, concentration independent transport coefficients, and no diffusive transport parallel to the membrane surface. For certain feed flow geometries and regimes this rigorous analysis of concentration polarization in reverse osmosis with low molecular weight feed solution constituents and without solute precipitation has been described in the literature.
Significantly more simple is the description of concentration polarization effects by the so-called film model. Considerations analogue to the heat transfer in turbulent and laminar feed flow conditions give quite accurate description of concentration polarization effects as function of the various process and membrane related parameters.

5.2.1.1 Concentration polarization in turbulent flow described by the film model
The film model assumes that even in turbulent feed flow, at a certain distance from the entrance a constant laminar boundary layer is established adjacent to the membrane surface in which longitudinal mass transport is negligibly low, so that mass transport within the film can be regarded to be one-dimensional in direction perpendicular to the membrane surface. During the filtration process, a steady state is reached where the convective transport of solutes to the membrane surface is counterbalanced by a diffusive flux of the retained material back into the bulk solution. Therefore a constant concentration profile of the retained material in the laminar boundary layer is obtained. This is illustrated in the schematic diagram of Figure 1.

![Diagram illustrating concentration profiles](image)

Fig. 5.1 Schematic diagram illustrating the concentration profiles of a component retained by the membrane and the fluxes in the laminar boundary layer at the feed side surface of a membrane under steady state conditions as assumed in the film model.
The material balance for the solute in the differential element of the film is given by:

\[ J_s = J_{s,\text{con}} - J_{s,\text{diff}} \quad (5.1) \]

Here \( J_s \) is the solute flux through the membrane, \( J_{\text{con}} \) is the solute flux toward the membrane by convection and \( J_{s,\text{diff}} \) is the solute flux from the membrane surface into the bulk solution by diffusion. Since furthermore:

\[ J_s = J_v C_s^p, \quad J_{s,\text{diff}} = -D_s \frac{dC_s}{dz} \quad \text{and} \quad J_{s,\text{convec}} = J_v C_s \quad (5.2) \]

\( J_v \) is the transmembrane volume flux, \( D_s \) is the diffusion coefficient and \( \frac{dC_s}{dz} \) is the concentration gradient of the solute in the boundary layer solution.

Combination of equations (5.1) and (5.2) and integrating with the boundary conditions: \( C_s = C_s^w \) at \( z = 0 \) and \( C_s = C_s^b \) at \( z = Z_b \) leads to:

\[ \frac{J_v Z_b}{D_s} = \ln \frac{C_s^w - C_s^p}{C_s^b - C_s^p} \quad (5.3) \]

Here \( Z_b \) is the boundary layer thickness and \( C_s^p \) is the permeate solute concentration.

The membrane rejection, \( R \), relates permeate and membrane wall solute concentration:

\[ R = 1 - \frac{C_s^p}{C_s^w} \quad (5.4) \]

Combination of equations (3) and (4) leads to:

\[ \frac{C_s^w}{C_s^b} = \exp \frac{J_v Z_b}{D_s} \frac{D_s}{R + (1 - R) \exp \frac{J_v Z_b}{D_s}} \quad (5.5) \]

In Equation (5.5) the concentration polarization is expressed as the ratio of the solute
concentration at the membrane surface $C_s^w$ and that in the bulk solution $C_s^b$. It is a function of the transmembrane flux, $J_V$, the thickness of the boundary layer, $Z_b$, the diffusion coefficient of the solute in the boundary layer solution, $D_s$, and the membrane solute rejection, $R$.

To describe the concentration polarisation under various feed flow conditions a solute mass transfer coefficient $k_s$ is introduced. Assuming that the transmembrane flux is small compared to the feed flow parallel to the membrane surface the mass transfer coefficient can be expressed by:

$$k_s = \frac{D_s}{Z_b} \quad (5.6)$$

Here $k_s$ is the solute mass transfer coefficient, $D_s$ is the solute diffusion coefficient in the boundary solution, and $Z_b$ is the boundary layer thickness.

Empirical correlation developed for various feed solution flow regimes under the assumption of steady state conditions can be used to estimate the mass transfer coefficient as a function of the feed flow velocity and filtration apparatus geometry. These correlation may be expressed in a very general form as:

$$N_{Sh} = aN_{Re}^b N_{Sc}^c \left(\frac{dH}{L}\right)^d \quad (5.7)$$

Here $N_{Sh}$, $N_{Re}$ and $N_{Sc}$ are respectively the Sherwood, the Reynolds and the Schmidt number; $dH$ is the hydraulic diameter or other characteristic dimension, $L$ is the length of the feed flow duct, which may be a channel or a tube; $a$, $b$, $c$, and $d$ are constants which are characteristic for different filtration system geometries and which must be experimentally determined.

The Sherwood number is given by:

$$N_{Sh} = k_s \frac{dH}{D_s} \quad (5.8)$$

The Schmidt number is given by:

$$N_{Sc} = \frac{\nu}{D_s} \quad (5.9)$$

The Reynolds number for turbulent flow in a tube or channel is given by:

$$N_{Re} = \frac{dHu}{\nu} \quad (5.10)$$
In a stirred batch cell the Sherwood and the Reynolds numbers can be expressed by the cell diameter $D_c$, the stirrer speed $\omega$ and the stirrer length $d$. Thus in a well stirred batch cell the Sherwood number is given by:

$$N_{Sh} = \frac{k_s D_c}{D_s}$$  \hspace{1cm} (511)

and the Reynolds by:

$$N_{Re} = \frac{\omega d^2}{\nu}$$  \hspace{1cm} (5.12)

Using the film model to describe concentration polarization in turbulent flow regime it is generally assumed that the flow is fully developed and entrance effect can be neglected. This can be done in most filtration systems that are used in large scale industrial applications therefore the exponent $d$ in Equation (5.7) is 0. In laminar the situation especially in modules consisting of relatively short thin channels. Here often the entrance length is covering the entire channel length.

Introducing Equations (5.9), (5.11) and (5.12) into Equation (5.7) gives the following relation for the mass transfer coefficient $k_s$ in a batch cell:

$$k_s = \frac{D_s}{D_c} a \left( \frac{\nu}{D_s} \right)^{0.33} \left( \frac{\omega d^2}{\nu} \right)^{0.66}$$  \hspace{1cm} (5.13)

Introducing Equation (5.13) into Equation (5.5) gives a relation for the concentration polarization in a well stirred batch cell:

$$\frac{C_s^w}{C_s^b} = \frac{\exp \frac{J \nu D_c}{aD_s \left( \frac{\nu}{D_s} \right)^{0.33} \left( \frac{\omega d^2}{\nu} \right)^{0.66}}}{R + (1 - R) \exp \frac{J \nu D_c}{aD_s \left( \frac{\nu}{D_s} \right)^{0.33} \left( \frac{\omega d^2}{\nu} \right)^{0.66}}}$$  \hspace{1cm} (5.14)

Here $C_s^w$ and $C_s^b$ are the solute concentrations at the membrane surface and in the bulk solution,
$D_s$ is the solute diffusion coefficient, $D_C$ is the diameter of the cell, $d$ is the stirrer length, $\nu$ is the viscosity of the solution, $\omega$ is the stirrer speed, $J_V$ is transmembrane flux, $R$ is the membrane rejection and $a$ is a constant which has a value between 0.1 and 0.6 depending on the cell and stirrer design.

Equation (5.14) shows that concentration polarization for a given feed solution and batch cell geometry is increasing with increasing transmembrane flux and membrane rejection and decreasing with increasing stirrer speed.

By introducing the appropriate relation for the hydraulic diameter and the length of the flow duct the concentration polarization can also be calculated for a rectangular channel and a circular tube. Concentration polarization in a rectangular channel is given by introducing Equations (5.6), (5.7), (5.8), (5.9) and (5.10) into Equation (5.5) with the hydraulic diameter expressed by the channel width, $w$ and the channel height, $h$ by:

$$d_H = \frac{2wh}{w + h} \quad (5.15)$$

Thus, the concentration polarization in a rectangular channel is given by:

$$\frac{C_s^w}{C_s^b} = \frac{\exp \left( J_V \frac{w h}{w + h} \right)^{0.2} \nu^{0.47}}{0.032D_s^{0.66}(u)^{0.8}} \frac{J_V \left( \frac{w h}{w + h} \right)^{0.2} \nu^{0.47}}{R + (1 - R)\exp \left( J_V \frac{w h}{w + h} \right)^{0.2} \nu^{0.47}} \frac{0.032D_s^{0.66}(u)^{0.8}}{0.032D_s^{0.66}(u)^{0.8}} \quad (5.16)$$

Here $w$ is the channel width and $h$ is the channel height and $u$ is the linear feed flow velocity.

The concentration polarization in a tubular membrane device can be calculated accordingly to:

$$\frac{C_s^w}{C_s^b} = \frac{\exp \left( J_{V_T} \right)^{0.2} \nu^{0.47}}{0.032D_s^{0.66}(u)^{0.8}} \frac{J_{V_T}^{0.2} \nu^{0.47}}{R + (1 - R)\exp \left( J_{V_T} \right)^{0.2} \nu^{0.47}} \frac{0.032D_s^{0.66}(u)^{0.8}}{0.032D_s^{0.66}(u)^{0.8}} \quad (5.17)$$

Here $r_T$ is the radius of the tubular membrane device.

5.2.1.3 Concentration polarization in laminar flow membrane devices
The film model which pictures a laminar boundary layer at the membrane surface and a turbulent mixed bulk solution can obviously not be applied to membrane devices with laminar feed flow conditions. The difference in the flow velocity profiles in laminar and turbulent flow are illustrated in Figure 5.2 which shows the flow velocity profiles in a channel with the channel height $<<$ as the channel width. In turbulent flow at the channel a laminar boundary layer is developed in which the flow velocity is increasing with the distance from the channel wall until it reaches the flow velocity of the bulk solution. The laminar boundary layers are comparatively thin compared to the channel height and a constant thickness of the laminar boundary layers is obtained a short distance from the channel entrance. This so called entrance length is short in turbulent flow devices and can in most technical relevant membrane modules be neglected. Thus, the film model can be applied assuming fully developed turbulent flow. In laminar the flow velocity is changing over the entire channel height with the highest velocity in the channel middle and the velocity profile is developed over a much longer distance from the channel entrance than in turbulent flow. Therefore, entrance effects can general not be neglected in most commercially available membrane modules operated with laminar feed flow when the concentration polarization effect are described mathematically. Although, the film model can not be applied in membrane devices operated in laminar flow concentration polarization can be calculated with reasonable accuracy by describing the mass transfer in analogy to the heat transfer in laminar flow by the Reynolds, the Schmidt, and the Sherwood number, taking the entrance length into account. The Sherwood number for laminar flow devices can be expressed by:

$$N_{Sc} = a \left( N_{Sc} N_{Re} \frac{d_H}{L} \right)^{0.33} \quad (5.18)$$
Fig. 5.2  Flow velocity profiles in turbulent and laminar flow

Introducing Equation (5.18) into Equation (5.5) the concentration polarization in laminar flow devices can be determined to a first approximation. For a more accurate calculation a rigorous treatment of concentration polarization involving the solution of the general transport equations for the solute, the continuity and the momentum.

For calculating the concentration polarization by applying the fil model in turbulent flow or by applying the heat transfer relations in laminar flow to the mass transfer in the more common filtration systems the characteristic constants are summarized in Table 5.1.
Tab. 5.1 Mass transfer correlation for the constants a, b, c, and d under various hydrodynamic feed flow conditions

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>Filtration device geometry</th>
<th>Hydraulic diameter $d_H$</th>
<th>Characteristic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Turbulent</td>
<td>tube</td>
<td>0.023</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>channel</td>
<td>0.023</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>stirred cell</td>
<td>0.05</td>
<td>0.7</td>
</tr>
<tr>
<td>Laminar</td>
<td>tube</td>
<td>1.86</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>channel</td>
<td>1.62</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>stirred cell</td>
<td>0.28</td>
<td>0.55</td>
</tr>
</tbody>
</table>

1) $r_t$ is the tube radius
2) h is the channel height and w is the channel width
3) $D_c$ is the diameter of the stirred cell and d is the stirrer length

Although the film model assumes several simplifications such as steady state conditions, that is no variations in the concentration profile with time, no mass transport parallel to the membrane surface due to concentration or density gradients; and fully developed velocity profile in the turbulent flow regime, Equation (7) has proved to be quite useful to describe the concentration polarization in reverse osmosis under various feed flow conditions.

5.2.2. Rigorous analysis of concentration polarization
The rigorous treatment of concentration polarization involves the solution of the general transport equations for fluid and solute, continuity and momentum. Treating the system two dimensional, i.e. considering only fluxes axial and vertical to the membrane surface concentration polarization can be described by the following relations:
Solute continuity relation (mass balance of solute)

\[
\frac{\partial C}{\partial t} = -v_z \frac{\partial C}{\partial z} - v_x \frac{\partial C}{\partial x} + D_z \frac{\partial^2 C}{\partial z^2} + D_x \frac{\partial^2 C}{\partial x^2}
\]  
(5.19)

Fluid continuity relation (mass balance of fluid)

\[
\frac{\partial \rho}{\partial t} + -v_z \frac{\partial \rho}{\partial z} - v_x \frac{\partial \rho}{\partial x} = 0
\]  
(5.20)

Momentum relation in axial direction

\[
\frac{\partial (\rho v_z)}{\partial t} + \frac{\partial (\rho v_x v_z)}{\partial x} + \frac{\partial (\rho v_z v_x)}{\partial z} = -\frac{\partial p}{\partial x} - \frac{\partial \tau_{zz}}{\partial x} - \frac{\partial \tau_{xz}}{\partial z}
\]  
(5.21)

Momentum relation in direction vertical to the membrane surface

\[
\frac{\partial (\rho v_z)}{\partial t} + \frac{\partial (\rho v_x v_z)}{\partial x} + \frac{\partial (\rho v_z v_x)}{\partial z} = -\frac{\partial p}{\partial z} - \frac{\partial \tau_{zz}}{\partial z} - \frac{\partial \tau_{xz}}{\partial x}
\]  
(5.22)

Here is C the solution concentration, \( \rho \) is the density of the feed solution, \( v \) is the velocity, \( p \) is the hydrostatic pressure, and \( \tau \) the shear stress tensor, \( z \) and \( x \) are directional co-ordinates referring in direction vertical and parallel to the membrane surface.

By introducing the proper boundary conditions and solving Equations (5.19) to (5.22) the distribution of solutes in the feed solution at the membrane surface and thus the concentration polarization can be determined. Unfortunately the solution of the couple continuity and momentum equations is mathematically rather complex and in general certain simplifications are introduced. In reverse osmosis for example, it can be assumed that viscosity changes due to concentration changes are small and can be neglected. Thus in reverse osmosis it can be assumed that the physical properties of the solution are constant and the velocity profiles are independent of solute mass transfer and solute concentration. With these simplifications several solutions of the continuity and momentum equations for determining the concentration polarization are suggested in the literature. Especially the ones developed by Sherwood and Brian for laminar
flow in thin channels are of technical relevance since in these cases the simple film model is difficult to apply.

The solution of the coupled momentum and continuity equations becomes significantly more complicated in the case concentration polarization leads to a precipitation of solutes at the membrane surface as is generally the case ultra- and microfiltration. Solutions of the coupled momentum and continuity equations in case of significant viscosity changes due to concentration polarization are also described in the literature.

5.2.3 Concentration polarization with solute precipitation at the membrane surface

In ultrafiltration and even more so in cross-flow microfiltration the simple film model is no longer applicable. This is because of two things: (1) The solutions treated contain macromolecular components or suspended materials. (2) The transmembrane fluxes are generally significantly higher than in reverse osmosis. In most cases due to the relatively low diffusion coefficient of macromolecules or even suspended particles the diffusive mass transport from the membrane surface back into the bulk solution is low and can not counterbalance the convective mass transport towards the membrane. Thus the solute concentration at the membrane surface exceeds the solubility of the feed solution constituents. This results in the precipitation of the feed solution constituents and the formation of a more or less dense layer on the membrane surface, which adds an additional hydrodynamic resistance to the transmembrane mass flux. The assumption that in the steady state the convective mass transport toward the membrane is always counter balance by the diffusive transport from the membrane into the bulk solution is no longer true when the membrane surface concentration has reached the solubility of the feed water constituents. In this case the concentration difference between the membrane surface and the bulk solution has reached its maximum value and the diffusive transport from the membrane surface into the bulk solution has also reached its maximum. If the transmembrane flux and thus the convective solute transport towards the membrane is increased by increasing the hydrostatic pressure more solutes are transported towards the membrane than can diffuse back. The additional solutes will also precipitate and increase the thickness of the layer at the membrane surface and thus increase its resistance correspondingly and in spite of an increase in the hydrostatic pressure driving force the transmembrane flux is not further increased. That means that in reverse osmosis and especially in ultrafiltration and cross-flow microfiltration of
solutions containing high molecular components with limited solubility the transmembrane flux will become independent of the hydrostatic pressure driving force as soon as these components precipitate and form a more or less solid layer at the membrane surface. Typical results obtained in ultrafiltration of macromolecular solutions that will precipitate at the membrane surface when a certain hydrostatic pressure or feed solution concentration is exceeded is shown in Figure 5.3. Here transmembrane fluxes obtained when filtering haemoglobin solutions of different concentrations through an ultrafiltration membrane are shown as a function of the applied hydrostatic pressure and the hemoglobin concentration.

Fig. 5.3 Transmembrane fluxes determined in a stirred batch cell at constant stirrer speed of 1800 revolutions per minute with pure water and haemoglobin solutions of various concentrations as a function of the applied hydrostatic pressure.

The filtration apparatus is a stirred batch cell operated at constant stirrer speed. With pure water the transmembrane flux is directly proportional to the applied hydrostatic pressure. With the haemoglobin solution is processed the transmembrane flux dependence on the applied pressure only at very low pressures and approaches a constant pressure independent value at higher pressures. This value is a function of the haemoglobin concentration and is lowest at the highest concentration. Similar transmembrane flux pressure relations are obtained in all filtration tests with feed solution that contain macromolecular or particulate components that have low diffusivities and thus tend to precipitate at the membrane surface. Under conditions of precipitation layer formation at the membrane surface the transmembrane flux can only be increased by a decrease
of the boundary layer thickness or the bulk solution concentration. The boundary layer in a membrane separation processes depends on hydrodynamic conditions of the system and depends on the degree of mixing, i.e. the Reynolds number achieved in the feed solution in turbulent flow or the channel height or capillary diameter under laminar flow conditions. The flux decline due to the formation of a precipitation layer depends furthermore on the feed water constituents. Some components, such as proteins or other biological components form rather dense layers effecting the transmembrane flux significantly while other materials such as rigid particles have a lesser effect on the flux.

The effect of the boundary layer thickness on the transmembrane flux has been demonstrated in several studies. It is also demonstrated in the graph of Figure 5.4 where the ultrafiltration flux of 1% bov. albumin (molecular weight 69,000) and 1% dextrane 110 (molecular weight 110,000) are shown as a function of the stirrer speed determined in a batch cell at 5 bar hydrostatic pressure. With increasing stirrer speed, that is decreasing boundary layer thickness, the transmembrane flux is increasing.

![Graph showing transmembrane fluxes](image)

**Fig.5.4** Transmembrane fluxes determined in a stirred batch cell with 1% solutions of dextrane 110 and bov. albumin at different stirrer speeds and constant hydrostatic pressure of 5 bar.

The experimental results show that in the case of precipitation of solute at the membrane surface, as e.g. in ultrafiltration and more so in cross flow microfiltration, the hydrodynamic resistance for membrane flux is not only a function of the membrane properties but is strongly effected by
the gel or cake layer, which is generally formed by the retained solutes at the membrane surface. To describe in this case the membrane flux/ feed solution concentration/applied pressure relation the rigorous approach based on the momentum and continuity equations is difficult to apply. Therefore, various models have been developed.

A very simple approach to describe the membrane flux in case of a gel or a cake layer formation is to neglecting the osmotic pressure of the feed solution, which can be done in many applications of in micro- and ultrafiltration, and expressing the flux in terms the resistances of the membrane and the layer in series according to the following relation:

\[ J_v = A \frac{1}{R_m + \eta \Delta z_l} \Delta p \]  

(5.23)

Here is \( J_v \) the transmembrane flux, \( R_m \) the hydrodynamic resistance of the membrane, \( r_l \) is the specific resistance of the layer, \( \Delta z_l \) is the thickness of the layer, \( \Delta p \) the hydrostatic pressure driving force and \( A \) is the membrane area.

The gel or cake layer formation in micro- and ultrafiltration is illustrated in Figure 5.5. This figure shows schematically a membrane, the gel layer at its surface and the concentration and hydrostatic pressure profiles in the bulk solution, the laminar boundary layer, the gel layer, and the membrane. The concentration of the retaint solute at the membrane surface \( C^W \) has reached the gel layer concentration which is the maximum value for the concentration polarization and thus also the maximum value for the diffusive transport of retaint components from the membrane back into the bulk solution. In the description of concentration polarization in terms of the film model it is assumed that diffusion is the only means for the transport of components away from the membrane surface back into the bulk solution, and that in steady state the diffusive transport is just counterbalanced by the convective transport towards the membrane. This means that an increase in the hydrostatic pressure will lead only to short lasting increase of the membrane flux and the convective transport of solutes towards the membrane surface. Since the diffusive transport from the membrane into the bulk solution is independent of the applied hydrostatic pressure and additional components transported towards the membrane surface will precipitate and lead to an increase in the gel layer thickness and the overall cake layer resistance will increase until the membrane flux has dropped back to its original value. This means that the
transmembrane flux in ultra- or microfiltration is independent of the applied hydrostatic pressure when a gel layer is formed due to precipitation of the retained components at the membrane surface and it depends only on the transport of these components back into the bulk solution.

Under conditions of precipitation of retained components at the membrane surface the membrane flux can only be increased by increasing the back transport of the retained components into the bulk solution. This can be done, e.g. by decreasing the boundary layer thickness, or decreasing the bulk solution concentration as can easily be seen from the Equation (5.5) which describes the mass in the laminar boundary layer in a filtration device with turbulent bulk flow. For simplicity it is assumed that the dissolved components are completely retained by the membrane, i.e. R = 1. Thus, is:

\[
\frac{C_s^w}{C_s^b} = \exp \frac{J_v Z_b}{D_s} \tag{5.24}
\]

Here \( C_s^w \) is the solute concentration at the membrane surface which identical the gel layer concentration and constant for a given temperature an pressure. With \( C_s^w = C_s^g = \text{constant} \) the flux is determined according to Equation (5.24) only by the bulk solution concentration and the
boundary layer thickness. It is for certain mass transfer condition and a given bulk solution concentration given by:

\[ J_v = \frac{D_v}{Z_b} \ln C_s^b = k_s \ln C_s^b \]  

(5.25)

In Figure 5.6 the membrane flux obtained for three different feed solution concentrations in filtration of solutions with constituents that precipitate at the membrane surface is shown as a function of the applied hydrostatic pressures as calculated by Equation (5.25).

---

![Flux versus pressure curves](image)

**Fig. 5.6** Schematic drawing showing the permeate flux as a function of the applied pressure for filtration of gel layer forming feed solutions of different concentrations

The flux versus pressure curves shown in Figure 5.6 show the same general pressure/flux relation as the experimental data obtain in ultrafiltration experiments with hemoglobin solutions of different concentrations and shown in Figure 5.3. The flux of pure water is linearly increasing with the applied pressure. The flux of a solution is also linearly increasing with pressure until a certain flux is obtained. A further crease in pressure does not lead to a permanent increase in flux since the concentration of the retained solutes at the membrane surface has reached the solubility limit and precipitation will occur. The precipitated solute will form a more or less dense layer
which will grow in thickness and in its hydrodynamic resistance when due to an increase in the applied pressure the flux through the membrane is increased for a short time period.

The gel or cake layer at the surface of a micro- or ultrafiltration membrane not only impairs the transmembrane flux, but it may also influence separation properties of the membrane. That is, the gel layer at the membrane surface can and often does act as a semipermeable membrane which retains lower molecular weight materials not rejected by the membrane. This is demonstrated in Figure 5.7 in which the retention of albumin in a mixture of bov. Albumin with γ-globulin in obtained in a batch cell filtration test using an Amicon Diaflo-XM 100 membrane is shown as a function of the applied hydrostatic pressure and the γ-globulin concentration. The stirrer speed was set at 1800 rpm. The bov.-albumine concentration was kept constant at 1 g per liter. If there is no γ-globulin or only a very low concentration the membrane which has a nominal molecular weight cut-off of 100 000 Dalton rejects no bov.-albumin. With increasing γ-globulin concentration and increasing applied hydrostatic pressure the bov.-albumin in more and more rejected. The reason for the bov.-albumin rejection is the formation of a gel layer at the membrane surface which apparently becomes with increasing γ-globulin concentration and increasing hydrostatic pressure dense enough to reject the bov.-albumin.

Especially in fractionation of biological fluid mixtures such as blood the formation of a gel layer impairs the entire process and can make an separation of different molecular weight components impossible.

Fig. 5.7 Retention of a Diaflo R–XM 100 membrane for bov.-albumin in a filtration test
carried out in a stirred batch cell at 1800 rpm at different applied pressure with a bov.-albumin/γ-globulin mixture of different globulin concentrations. The albumin concentration was constant and 1 gL⁻¹.

With the formation of a gel or cake layer during filtration of macromolecular, or particular solution or suspension with high flux membranes, a mathematical modeling of the process becomes significantly more complex. Because the specific resistance of the gel layer depends on the layer forming components and can be very different for different components. While some rigid materials such as latex balls form layers that resemble the packing of ridged spheres do other materials such as certain proteins or dextran form gel-type layers and certain oil emulsions dense oil films at the membrane surface which have an extremely high specific resistance to the permeation of water. Many gel layers change their structure with time and their resistance is often increasing with time.

Furthermore, because of the low diffusivities of macromolecules and particles, diffusion can no longer be the only means of transportation of the components retained by the membrane in micro- and ultrafiltration. Grossly simplified, the process can be described as a three step procedure as indicated in the schematic diagram of Figure 5.8. In the gel layer the material retained by the membrane is more or less solidly integrated in a structure. The strength of this structure will depend on the intrinsic properties of the material but also on the hydrostatic pressure and eventually on the "age" of the gel layer. The first step in the process of bringing the material back into the bulk solution therefore is to release it from the structure into the solution of the boundary layer. If the material is in solution it can diffuse or be transported by „other means“ such as by convection into the bulk solution. Step 2 and 3 of the transport process are in parallel, while step 1 and 2 or 3, respectively, are in series.
In parallel processes, the fastest is the overall rate determining step and in consecutive processes the slowest is rate determining. In Ultra- and microfiltration with gel layer formation it is quite likely that the first step, that is, the release of the material from the gel layer structure, is the rate determining step and from the two parallel steps the convective transport is fastest.

There are several experimental results published in the literature supporting the assumption that the release of the material from the gel structure is the rate determining step for the transport of macromolecular or particulate material from the membrane surface into the bulk solution. For instance, in almost all ultrafiltration tests a flux decline with time is observed even when all other operating parameters are kept constant. The original transmembrane flux can usually be restored when the membrane has been cleaned thoroughly with a proper solution. This is demonstrated in Figure 5.9 where the results of a cheese whey filtration test is shown.

The flux decline with time when all operating parameters are kept constant, such as shown in Figure 5.9 and observed in many practical ultrafiltration tests, is difficult to explain with flow
condition arguments only. It can, however, be rationalized by the assumption that the rate limiting step for the transport of the material retained at the membrane surface into the bulk solution is the release rate of the material out of the gel structure. This rate may well decrease with time when the gel structure is aging and is becoming more compact under pressure.

Mathematically modeling the mass transport at the membrane surface in micro- and ultrafiltration in terms of the hydrodynamic feed flow conditions, which includes all phenomena observed in practical separation problems is rather difficult when a gel layer has been formed. Based on the film model the transmembrane flux can be described as shown earlier by:

\[ J_v = k_s \ln C_s^b \]  

(5.26)

The mass transfer coefficient \(k_s\) at the membrane surface in a gel layer controlled filtration process is no longer just a function of the diffusion coefficient and boundary layer thickness, but depends also strongly on the shear rate at the membrane surface and the chemical and mechanical properties of the gel layer, which may change with time due to compaction and aging.

In the literature, there are numerous publications in which experimentally determined transmembrane fluxes have been correlated with various hydrodynamic feed flow parameters. It seems that a correlation of the transmembrane flux with the average shear rate at the membrane surface is quite satisfactory for many practical applications. This seems reasonable, if the release of the material from the gel layer is assumed to be the rate limiting step for the mass transport from the membrane surface into the bulk solution.

\textit{Mathematical description of gel layer formation and its consequences}

For feed solutions with low molecular weight constituents and without solute precipitation the mass transport at the membrane surface can be well described by the film model or by a numerical integration of the transport equations for fluid and solutes, i.e. the material and momentum balance combined with the corresponding laws of diffusion for the solute and the solvent. The mathematical description of the mass transport at the surface in ultra- and microfiltration of solutions with macro-molecular solutes and varying viscosity in the laminar boundary layer is significantly more difficult because multitude of process parameters and their interdependency which must be considered and which are specific and eventually very different
for different components of a mixture. Many attempts to model the flux/pressure relation in ultra- and microfiltration when gel layers have been formed at the membrane surface are described in the literature. Many of these models use fitting parameters and can be applied only to very specific conditions of membranes, feed solutions and process parameters. A general model that fits all feed solutions and process parameters seems to be too complex to be of practical value.

5.2.4 Membrane fouling and its causes
Discussing membrane processes in the literature often the term "membrane fouling" is used to describe a long-term flux decline caused by accumulation of certain materials at the membrane surface. The consequences of membrane fouling are rather obvious; its causes, however, often not very clear. The formation of a gel or cake layer formation is one cause for membrane fouling. Gel or cake layer formation may be caused by a variety of materials including inorganic precipitates such as CaSO₄, Fe(OH) and other metal hydroxides, organic materials such as proteins, humic acids and other macromolecular materials, and biological components such as micro-organisms and products of their metabolism. Membrane fouling may also occur without concentration polarization, i.e., a direct transport to the membrane as surface in any mass separation process. The attachment of the substances to the membrane surface may be caused by adsorption due to hydrophobic interactions, van der Waals force attractions, or electrostatic forces. The fouling layer itself may be rather porous and thus permeable for aqueous solutions as some inorganic precipitants or highly impermeable as some films of mineral oils or hydrophobic surfactants. The fouling mechanism depends also on the membrane process. In electrodialysis fouling is caused mainly by the precipitation of polyelectrolytes or sparingly soluble salts such as CaSO₄ or CaCO₃. Membrane fouling in electrodialysis effects mainly the anion-exchange membranes because most of the colloidal and macromolecular poly electrolytes present in natural waters such as humic acids or proteins are negatively charged. In ultra- and microfiltration of biological solutions but also in reverse osmosis of sea water biological fouling is a severe problem affecting the economics of the processes. In biomedical applications protein adsorption and protein denaturation at the membrane surface is often impairing the performance of the membranes.

The difference between concentration polarization and membrane fouling or scaling is shown
schematically in Figure 5.10. Concentration polarization is a reversible process based on diffusion and takes place over a few seconds it can be described adequately by a simple mathematical model and easily be controlled by the proper process design. Fouling is generally irreversible and the flux decline takes place over many minutes, hours or even days. A constant flux is generally not reached at all. Membrane fouling is more difficult to describe and to control by experimental means. Membrane fouling is determined by a variety of different parameters including the feed solution constituents and their concentration, membrane material, and the fluid dynamic system design. Membrane fouling can be caused by simple precipitation of insoluble materials or reversible and irreversible adsorption of components at the membrane surface and within the membrane pores.

![Diagram showing flux decline due to concentration polarization and membrane fouling](image)

Fig 5.10 Schematic diagram illustrating the difference between the flux decline due to concentration polarization and due to membrane fouling

**Prevention of membrane fouling**

The means of preventing or at least controlling membrane fouling effects are as heterogeneous as the different material and mechanisms causing the fouling. The main procedures to avoid or control fouling involve

1. pretreatment of the feed solution,
2. membrane surface modifications,
3. hydrodynamic optimization of the membrane module, and
4. membrane cleaning with the proper chemical agents.

A pretreatment of the feed solution may included chemical precipitation, prefiltration, pH-adjustment, chlorination or carbon adsorption. In some membrane module design concepts as for instance in hollow fiber modules the elimination of all particulate materials is of great
importance for the proper function of the membrane. Membrane surface modifications include the introduction of hydrophilic moieties or charged groups in the membrane surface by chemical means or plasma deposition. Increasing the shear rate imposed by the feed solution on the membrane surface will in many cases reduce the membrane fouling. High feed flow velocities and the proper module design are efficient tools in controlling membrane fouling. When in spite of an adequate membrane and module design the transmembrane flux is decreasing with operation time to an unacceptable low value it is necessary to clean the membrane to restore the flux in part or completely. Typical cleaning agents are acids and bases, such as HNO$_3$ and NaOH, complexing agents as ethylene-diamine-tetra-acetic-acid, enzymes, detergents, and desinfectants. Another very effective method to minimize the effects of membrane fouling in microfiltration is back flushing. In back flushing the applied pressure is reversed and the permeate pushed through the membrane lifting of any fouling material that had been precipitated on the feed side membrane surface and washing it out of the filtration device. Back flushing is usually done in certain time intervals for a couple of seconds. It will be discussed in more details later.

5.3 Concentration polarization in other membrane separation processes In other membrane separation processes of technical relevance concentration polarization is of lesser significance than in reverse osmosis or ultrafiltration. It can generally be controlled and its detrimental effects be minimized with the proper process design.

5.3.1 Concentration polarization in dialysis In dialysis concentration polarization is an accepted phenomenon. There will always be a depletion of the components in the boundary layer at the membrane surface facing the feed solution and an accumulation at the membrane surface facing the dialysate, as indicated in Figure 5.11. However, the differences between the membrane surfaces and the bulk solutions concentrations is low, because dialysis membranes are rather thick compared to the laminar boundary layers at their surfaces and the transport within the membrane will be rate limiting for the overall mass transfer from the feed to the dialysate bulk solutions. Thus, in dialysis concentration polarization effects will be small.
5.3.2 Concentration polarization in electrodialysis

In electrodialysis concentration polarization has two affects: It leads to a decrease of the ion concentration at the membrane surface facing the diluate cell and to a concentration increase at the membrane surface facing the concentrate cell of the electrodialysis stack. The concentration increase may lead to a precipitation of salts. The concentration decrease is decreasing the limiting current density. The effects of concentration polarization in electrodialysis and its consequences for the limiting current density and the overall process economics will be discussed in detail later. It is controlled by the cell design and the flow velocities in the system minimizing the thickness of the laminar boundary layers at the membrane surfaces.

5.3.3 Concentration polarization in pervaporation

In pervaporation concentration polarization can occurs on both sides of the membrane. As in dialysis the boundary layer at the membrane surface facing the feed solution will be depleted of the preferentialy permeating components, which will then be enriched at the membrane surface facing the permeate. In pervaporation concentration polarization is generally controlled by decreasing the laminar boundary layer thickness through hydrodynamic measures. This can lead to problems when high flux thin film composite membranes are used. At the permeate side the laminar boundary layer is always as thick as the porous substructure and severe concentration polarization as well as capillary condensation may occur on the permeate side of the membrane.

Fig. 5.10 Schematic diagram illustrating the effects of concentration polarization in dialysis
If the solubility of the permeating component in the feed solution is low the boundary layer at the feed side of the membrane may be depleted of the permeating component and the transmembrane flux as well as the separation efficiency may be severely impaired. This, e.g. is the case when organic solvent/water mixtures of limited solubility are treated.

5.3.4 Concentration polarization in gas separation
In the separation of gases by solution-diffusion membranes concentration polarization is of lesser importance and has generally little effect on the overall efficiency of the process. The reason is that the diffusivity of gases in the gas phase is much higher than in a solid polymer phase. Therefore, the transport rates in the boundary layer are comparatively high and there is hardly any cumulation or depletion of components at the membrane surface.
6. Membrane Separation Processes as Unit Operation

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Summary
In this chapter technically relevant membrane separation processes are treated as unit operation. Their basic principles and various commonly applied operation modes are described. The theoretical and practical limitations of the various processes in different applications due to membrane properties or due to the system design is discussed and their technical and economic advantages of the processes compared to other competing processes are pointed out. The possibility of combining processes which have different ranges of optimum efficiencies for a given separation tasks as so-called hybrid processes is discussed in selected examples.
6.1 General considerations

As pointed out earlier, membrane separation processes can differ greatly in the membranes and driving forces used for separation, the process design, the area of application and in their technical and economic relevance. Table 6.1 gives a summary of technically relevant membrane separation processes, the membrane type used in these processes, their operating principles, and their main areas of application. The driving forces applied for the transport of the various components through the membrane are hydrostatic pressure differences and chemical or electrochemical potential gradients across the membrane which may be expressed in concentration differences, partial pressure differences or electrical potential differences between two solutions separated by a membrane. The efficiency of a separation in a given membrane process, however, is not only determined by the membrane properties, it also depends on the applied driving force or forces. In membrane separation processes components are generally concentrated in the so-called retentate and depleted in the permeate. The maximum or minimum concentrations that can be achieved in the retentate or the permeate, respectively, depend not only on the membrane properties but are also affected by the process design especially by the recovery rate of the original feed mixture. The same is true for the loss of produce which shall be recovered in the retentate when the membrane is not strictly semipermeable. For economic reasons, should the recovery rate in a membrane process always be as high as possible. In treating the various membrane processes as unit operations a relation between the recovery rate and various process parameters such as the concentration of the different components in the feed, in the retentate and in the permeate must be developed. Concentration polarization and membrane fouling effects must be considered and a process must be optimized for a certain application in terms of its energy efficiency and overall costs.
Table 6.1 Technically relevant membrane separation processes, their operating principles, and their application

<table>
<thead>
<tr>
<th>separation process</th>
<th>membrane type used</th>
<th>applied driving force</th>
<th>mode of separation</th>
<th>applications</th>
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<tr>
<td>microfiltration</td>
<td>symmetric porous structure, pore radius 0.05-5 µm</td>
<td>hydrostatic pressure 0.5-4 bar</td>
<td>filtration (size exclusion)</td>
<td>water purification, sterilization</td>
</tr>
<tr>
<td>ultrafiltration</td>
<td>asymmetric porous structure, pore radius 2-10 nm</td>
<td>hydrostatic pressure 1-10 bar</td>
<td>filtration (size exclusion)</td>
<td>Separation &amp; fractionation of molecular mixtures</td>
</tr>
<tr>
<td>diafiltration</td>
<td>asymmetric porous structure, pore radius 2-10 nm</td>
<td>hydrostatic pressure 1-10 bar</td>
<td>filtration &amp; dialysation (size exclusion)</td>
<td>purification of molecular mixtures artificial kidney</td>
</tr>
<tr>
<td>reverse osmosis</td>
<td>asymmetric skin-type solution-diffusion structure</td>
<td>hydrostatic pressure 10-100 bar</td>
<td>solution-diffusion mechanism</td>
<td>sea &amp; brackish water desalination</td>
</tr>
<tr>
<td>dialysis</td>
<td>Symmetric porous or gel-type structure</td>
<td>concentration gradient</td>
<td>diffusion</td>
<td>artificial kidney</td>
</tr>
<tr>
<td>electrodialysis</td>
<td>symmetric ion-exchange membrane</td>
<td>electrical potential</td>
<td>migration Donnan-exclusion</td>
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<tr>
<td>donnan dialysis</td>
<td>symmetric ion-exchange membrane</td>
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<td>electrodialytic water dissociation</td>
<td>bipolar membrane</td>
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<td>acid &amp; base production from salts</td>
</tr>
<tr>
<td>gas separation</td>
<td>homogeneous symmetric structure</td>
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<td>oxygen/nitrogen separation</td>
</tr>
<tr>
<td>pervaporation</td>
<td>homogeneous symmetric structure</td>
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<tr>
<td>vapor permeation</td>
<td>homogeneous symmetric structure</td>
<td>vapor pressure gradient</td>
<td>solution-diffusion</td>
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</tr>
<tr>
<td>membrane distillation</td>
<td>symmetric porous hydrophobic</td>
<td>vapor pressure</td>
<td>diffusion</td>
<td>liquid/solid separation</td>
</tr>
</tbody>
</table>
6.2 Pressure driven membrane processes

Typical pressure driven membrane processes are microfiltration, ultrafiltration, and reverse osmosis. The principle of these processes is illustrated in the schematic drawing of Figure 6.1.

Microfiltration, ultrafiltration and reverse osmosis are basically identical processes and differ only in the sizes of the particles to be separated and the membranes which are. In all three processes, a mixture of different components is brought to the surface of a semipermeable membrane. Under the driving force of a hydrostatic pressure gradient, some components permeate the membrane while others are more or less completely retained. Thus, in reverse osmosis or ultra- and microfiltration, a feed solution is separated into a filtrate which is depleted of particles or molecules and a retentate in which these components are concentrated. The term microfiltration is used when particles with diameters in the range of 0.1 to 10 µm are separated from a solvent or other components of low molecular weight. The separation mechanism in microfiltration is based on a sieving effect and particles are separated solely according to their dimensions. The membranes used for microfiltration are symmetric microporous structures with pore sizes in the range of 0.1 to 10 µm. The hydrostatic pressure difference used as driving force in microfiltration is in the range of 0.5 to 4 bars.
The separation process is called ultrafiltration when the components to be retained by the membrane are true molecules or small particles not larger than 0.1 µm in diameter. This roughly corresponds to the limit of resolution obtainable in an optical microscope. In ultrafiltration, where generally the osmotic pressure of the feed solution is negligibly small, hydrostatic pressures of 2 to 10 bars are used. Ultrafiltration membranes are mostly asymmetrically structured with pores having a diameter of 4 to 50 nm in a skin layer at the membrane surface facing the feed solution.

In reverse osmosis low molecular weight compounds, such as salts, sugars etc. are separated from a solvent, usually water. Feed solutions, therefore, often have significant osmotic pressures which must be overcome by the hydrostatic pressure applied as driving force. As shown earlier, the transmembrane flux is according to Equation (2.161) a function of the hydrodynamic permeability of the membrane, and a net pressure difference, i.e. the hydrostatic pressure difference between feed- and filtrate solution minus the difference in osmotic pressure between the feed and filtrate solutions. The osmotic pressure of a solution containing low molecular weight solutes, such as salts or sugar etc., can be rather high, even at relatively low solute concentrations. The osmotic pressure for sea-water, for instance, is about 25 to 28 bars. The osmotic pressure of orange juice is between 25 and 30 bars. The osmotic pressure which has to be overcome by the applied hydrostatic pressure limits the practical application of reverse osmosis.

Gas permeation is in many aspects similar to reverse osmosis. In both processes asymmetric solution diffusion-type membranes and a hydrostatic pressure driving force are used for the transport of different components through the membrane. The selectivity of which is also determined by the solubility and diffusivity of the different components in the membrane. In contrast to reverse osmosis, where liquid mixtures are separated, in gas permeation, the feed mixture to be separated consists of gases or vapors. The terminology used in gas permeation to describe the separation properties of the membrane or the process is also different to those used in reverse osmosis and will be discussed separately.

6.2.1 Pressure driven membrane processes as unit operation

Today, the most relevant pressure driven processes are ultra- and microfiltration and reverse osmosis. Their basic operating principle is illustrated in Figure 6.1. It shows a membrane in a filtration unit converting a feed mixture under the driving force of a hydrostatic pressure gradient.
into a retentate and a filtrate. For simplicity, both the retentate and the filtrate are assumed to be well mixed and to have no concentration gradients.

When the feed mixture of molecules and particles is brought to the surface of a semi-permeable membrane by convection the solvent and/or small solutes pass the membrane as filtrate under a hydrostatic pressure driving force, while larger particles and molecules are retained by the membrane and concentrated in the retentate.

The performance of a membrane in a pressure driven separation process is determined by its filtration rate, i.e. the transmembrane flux at a certain hydrostatic pressure driving force and its mass separation properties, that is its capability to retain certain components of a mixture. The filtration rate or transmembrane fluxes in microfiltration, ultrafiltration and reverse osmosis can be described respectively by the equations (2.126), (2.131) and (2.161), as discussed in the previous section of this outline. In a more general relation the membrane flux properties in pressure driven membrane processes can also be expressed by a hydrodynamic resistance of the membrane matrix, i.e.:

\[ J_V \approx \frac{1}{R_M} \]  

(6.1)

Here \( J_V \) is the filtration rate and \( R_M \) is the hydrodynamic resistance of the membrane.

### 6.2.1.1 Recovery rate, membrane retention, and retentate and filtrate concentrations

The separation capability of a membrane in reverse osmosis or ultra- and microfiltration can be expressed in terms of a membrane retention or rejection, which is defined as:

\[ R = 1 - \frac{C_s^f}{C_s^r} \]  

(6.2)

Here \( R \) is the retention of the membrane for a given component \( s \) under certain operating conditions of hydrostatic pressure and feed solution concentration. \( C_s^f \) and \( C_s^r \) are the concentrations of the retained component, \( s \) in the filtrate and the retentate, respectively. Because of the osmotic pressure, the viscosity, etc., the concentration in the retentate in reverse osmosis or ultra- and microfiltration cannot exceed a certain maximum value. The solvent of the feed solution can, therefore, never be completely recovered as filtrate.
The part of the feed solution that can be recovered as filtrate, i.e. ratio of the filtrate volume to that of the feed solution volume is referred to as the recovery rate, \( \Delta \) which is given by:

\[
\Delta = \frac{V_f}{V_o}
\] (6.3)

Here \( V_f \) and \( V_o \) are the volume of the filtrate and the feed solution, respectively.

The recovery rate is an operational variable, which is not linked to membrane properties.

The concentrations in the retentate and the filtrate are not only determined by the membrane rejection but they are also a function of the recovery rate. The relation between concentration of the retentate, the filtrate, the feed solutions, the membrane rejection and the recovery rate can be determined from a simple mass balance. If complete mixing of the retentate solution is assumed, the concentration of a component in the retentate is given by:

\[
C^r_S = C^o_S (1 - \Delta)^{-R}
\] (6.4)

Here \( C^o_S \) is the initial concentration of the feed solution and \( C^r_S \) the retentate concentration, \( \Delta \) is the recovery rate and \( R \) the membrane retention.

The concentration in the filtrate is directly proportional to that in the retentate and given by:

\[
C^f_S = (1 - R)C^r_S
\] (6.5)

Thus, for a given recovery rate is the filtrate concentration at any given time found by introducing Equation (6.4) into equation (6.5):

\[
C^f_S = C^o_S (1 - R)(1 - \Delta)^{-R}
\] (6.6)

Here \( C^o_S \), \( C^r_S \) and \( C^f_S \) are the concentrations of the feed solution, the retentate and the filtrate, respectively, at a given time during the filtration process. \( R \) is the rejection of the membrane and \( \Delta \) the recovery rate achieved during a given time.

It should be noted that the filtrate concentration expressed in Equation (6.6) is the concentration corresponding to a given recovery rate, i.e. determined during an infinitely small time interval at a given recovery rate. For most practical application, however, the filtrate concentration obtained at an infinitely small time interval at a certain recovery rate is of less interest than the so-called "mixing cup" concentration, which is obtained when the entire filtrate up to a given recovery
rate, is collected and mixed. The mixing cup filtrate concentration can be calculated by the following relation, which is obtained from a mass balance and Equations (6.3) and (6.5). The mass balance for the total process is:

\[ V_o C_s^o = V_r C_s^r + V_f C_s^f \]  \hspace{1cm} (6.7)

Introducing Equations (6.3) and (6.5) leads to:

\[ C_s^f = \frac{C_s^o}{\Delta} \left[ 1 - (1 - \Delta)^{1-R} \right] \]  \hspace{1cm} (6.8)

Here \( C_s^f \) is the mixing-cup concentration.

The mixing cup concentration is always lower than the concentration obtained during an infinitely short time period at a certain recovery rate. The relation between the recovery rate, the membrane rejection, the retentate, the filtrate and the mixing cup concentration is illustrated in Figure 6.2, where the retentate, the filtrate, and the mixing cup concentrations are each shown as a function of the recovery rate for three different membrane rejection coefficients.
Fig. 6.2  a) Ratio of retentate to feed solution concentration, b) filtrate to feed solution concentration and c) "mixing cup" filtrate to feed solution concentration as a function of the recovery rate calculated by equations (6.4), (6.7) and (6.8), each for three different membrane solute rejections.

In membrane evaluation or characterization tests, the rejection of a membrane is generally calculated from the mixing cup filtrate and the retentate concentration, two experimental values which can easily be measured by rearranging Equation 6.8:
Here R is the membrane rejection, $C_s^f$ and $C_s^o$ are the mixing cup filtrate and the feed solution concentrations, respectively, and D is the recovery rate.

The significance of the mixing cup and maximum retentate concentration can be illustrated in practical examples. For instance, in the production of potable water from sea or brackish water the concentration in the filtrate should not exceed 500 mg total dissolved solutes per liter. This concentration is the filtrate collected over a certain time and recovery rate, i.e. the mixing cup concentration.

For economic reasons the recovery rate should always be as high as possible. Often, however, the recovery rate of a given feed solution is not only limited by the maximum value of the mixing cup concentration of the filtrate. If the feed solution contains solute with limited solubility, e.g. salts such as CaSO4 or CaCO3, the recovery rate is determined by the maximum retentate concentration achievable without solute precipitation and that is the maximum retentate concentration at a given recovery rate.

### 6.2.1.2. Solute losses in membrane filtration processes

In a membrane filtration process the “product” may be either the filtrate (as in the production of ultra pure or sterile water) or the retentate (as in the concentration of proteins from whey). For membranes, which are not strictly semi-permeable, i.e. membranes which have a solute rejection of less than 100 %, some solutes will be found in the filtrate. This might effect the quality of the filtrate, which for example may be ultrapure water, or may lead to product losses, when protein are recovered from whey by filtration.

The fractional solute loss is usually expressed by the ratio of solute lost with the filtrate divided by the total amount of solutes in the feed solution. The fractional solute loss is calculated from a mass balance between the feed solution and the filtrate and introducing Equation (6.7) It is given by:

$$\delta = \frac{V_f C_s^f}{V_o C_s^o} = 1 - (1 - \Delta)^{1-R}$$

(6.10)
Here $\delta$ is the fractional solute loss, $V_f$ and $V_o$ are the volumes of the filtrate and the feed solution, $C_s^f$ and $C_s^o$ are the mixing cup filtrate and the initial feed solution concentrations. $\Delta$ is the recovery rate, and $R$ is the membrane rejection.

The product loss may be significant even with membranes that have a relatively high solute rejection, when high retentate concentrations are desired, as indicated in Figure 6.3. Here fractional solute loss is shown as a function of the recovery rate for different membrane rejection.

![Graph showing fractional solute loss in membrane filtration](image)

**Fig. 6.3** Fractional solute loss in membrane filtration, calculated for different membrane rejection by Equation (6.10), shown as a function of the recovery rate.

### 6.2.1.3 The osmotic pressure and energy requirements in membrane filtration processes

The minimum energy required in a membrane filtration process is given by the Gibb’s free energy of mixing the filtrate and retentate solutions, which is given by:

$$
\Delta G^m = G' - G'' = \sum_i (\mu'_i d_{n_i}^i = \mu''_i d_{n_i}''') \equiv RT \sum_i \Delta n_i \ln \frac{a'_i}{a''_i} \quad (6.11)
$$

Here $\Delta G^m$ is the Gibb’s free energy of mixing two solutions indicated by ‘ and “, $\mu$ is the chemical potential, $a$ the activity and $n$ the number of moles, the subscript $i$ refers to individual components.
If it is assumed that the membrane is permeable for the only solvent then the Gibb’s free energy can be expressed by chemical potential of the solvent which is related to the osmotic pressure of the solutions.

The osmotic pressures of the solution is:

\[ \pi = \frac{RT \ln a_w}{V_w} \]  
(6.12)

Here the subscript refers to the solvent.

Introducing Equation (6.12) into Equation (6.11) leads to:

\[ \Delta G^m = \Delta n_w V_w \Delta \pi \approx V_f \Delta \pi \]  
(6.13)

Here \( \Delta \pi \) is osmotic pressure difference between the two solutions ‘ and “ separated by the membrane and \( V_w \) and \( V_f \) are the partial molar volume of the solvent and the filtrate volume, which is for a dilute solution is to a first approximation given by \( \Delta n_w V_w \approx V_f \).

The energy required in pressure driven processes in a practical application for the separation of various components is always higher than the theoretical minimum due to irreversible friction energy which is lossed when the individual molecules move through the membrane matrix and when the pressurized retentate is brought back to atmospheric pressure by forcing it through a pressure relieve valve. Thus, the total energy consumed in a pressure driven filtration process is given by the applied hydrostatic pressure multiplied by the filtrate volume and if there is no energy recovery system by the volume of the retentate.

\[ \Delta E_{tot} \approx V_f (\Delta p - \Delta \pi) + V_t \Delta p \]  
(6.14)

The basic difference between reverse osmosis and ultra- or microfiltration, as pointed out before, is the size or molecular weight of the solutes which are separated from a solution.

In reverse osmosis low molecular weight components, such as salts, sugars, etc. are separated from a solvent and the feed solution has a significant osmotic pressure, which has to be overcome by the hydrostatic pressure applied as driving force while in ultra- and especially in microfiltration macromolecular components or particles are retained by the membrane and the solutions have generally negligibly low osmotic pressures.
6.2.1.4 Diafiltration

A variation of the ultrafiltration process, generally referred to as diafiltration, is often used when a more complete separation of micro- and macrosolutes from a mixture is required. This process, which competes directly with dialysis, is shown schematically in Figure 6.4.

\[ \text{dilution (} V_w \text{)} \]

\[ \text{feed solution (} V_o C_0 \text{)} \]

\[ \text{membrane} \]

\[ \text{diafiltrate (} V_f C_f \text{)} \]

Fig. 6.4 Schematic diagram illustrating the operating mode of diafiltration

The schematic diagram shows a batch-type ultrafiltration system containing a mixture of various macro- and microsolutes. The membrane to be used in diafiltration should retain the macromolecular components more or less completely and should not reject the microsolutes. If the filtrate removed from the cell is replaced by pure solvent the low in molecular weight constituents will gradually be washed out of the feed mixture. The concentration of the various components in the diafiltration vessel at any time can be calculated by a mass balance. If the volume of the original solution is kept constant and identical to the volume of the diafiltration vessel, the concentration in the diafiltration vessel can then be calculated as a function of the membrane retention and the volume of the diafiltration washing solution, i.e. the pure solvent replacing the filtrate volume.

The concentration change in time in the filtrate is given by:

\[ dV_f C_f = -V_o dC_s \]  \hspace{1cm} (6.15)

Furthermore is:
\[ V_f = V_w \quad (6.16) \]

and

\[ C_s^f = (1 - R)C_s^0 \quad (6.17) \]

Here \( V_w, V_f \) and \( V_w \) are the volume of the feed solution, the filtrate and the added wash solution, \( C_s^f \) and \( C_s^0 \) are concentrations in the filtrate and the diafiltration vessel at a certain time \( t \) and \( R \) is the membrane retention.

Introducing Equations (6.16) and (6.17) into Equation (6.15) and integrating with the boundary conditions: \( t = 0, C_s^f = C_s^0 \) and \( V_w = 0 \) and leads to: \( t = t, C_s^t = C_s^f \) and \( V_w = V_w \).

\[ \frac{C_s^f}{C_s^0} = \exp \left( -\frac{V_w}{V_o} (1 - R) \right) \quad (6.18) \]

Here are \( C_s^f \) and \( C_s^0 \) the concentrations in the diafiltration vessel at the time \( t \) and the feed solution at the beginning of the filtration, respectively. \( V_o \) is the volume of the diafiltration vessel, \( V_w \) is the volume of solvent added at time \( t \), and \( R \) is the rejection of the membrane for the component under consideration.

If the component is completely retained by the membrane, i.e \( R = 1 \), its concentration in the batch cell will not change. If the component passes the membrane unaffected, i.e. \( R = 0 \), its concentration in the diafiltration vessel will decrease according to the exponential function expressed in Equation (6.18). The “wash-out effect” obtained in diafiltration is illustrated in Figure 6.5, where the retentate concentration is shown as a function of the ratio of rinse to feed solution volume for various membrane rejections.
If the a macromolecular component is only partially rejected by the membrane, a substantial loss of product will be encountered. If complete removal of a components the low in molecular weight without substantial loss of macromolecular material is desired, rejection of the membrane should be close to zero for the component low in molecular weight, and close to one for the macromolecular component as shown in Figure 6.5.

6.2.1.5 Product loss in diafiltration

As in ultrafiltration, product losses in diafiltration may be significant when, e.g., in a process of desalting a macromolecular solution, the membrane does not reject the macromolecules completely. The product loss $\delta$ is then given by:

$$\delta = \frac{V_f C_f^o}{V_o C_s^o}$$  \hspace{1cm} (6.19)

Introducing the mass balance and combining Equation (6.17), (6.18) and (6.19) and rearranging gives the product loss in diafiltration as function of the wash solution volume, the diafiltration vessel volume and the membrane retention.
Here $\delta$ is the fractional product loss, $V_o$, and $V_w$ are the volumina of the diafiltration vessel, the filtrate and the wash solution, R is the membrane rejection.

In Figure 6.6 the fractional product loss is shown as a function of the ratio of feed solution and wash solution volume for membranes with different rejection characteristics as calculated from Equation (6.20).

$$\delta = 1 - \exp\left(-\frac{V_w}{V_o} (1 - R)\right) \quad (6.20)$$

Fig. 6.6 Fractional product loss in diafiltration calculated by Equation (6.20) for various solute rejections

As can easily be seen from Figures 6.5 and 6.6, the concentration of a low molecular weight solute is reduced to less than 1 % of its original value by wash solution volume 5 times that of the feed solution volume, when the membrane passes the solute unhindered, i.e., $R = 0$. If the solute is partially rejected by the membrane correspondingly more wash solution is needed to reduce the concentration of the low molecular weight solute below a certain value. On the other
hand when the membrane rejects the macro solute completely, no product is lost, but partial rejection leads to a significant product loss.

6.2.2 Gas separation

Separation of gases can be achieved in microporous as well as in homogeneous membranes. The selectivity of microporous membranes for different membranes is because of the Knudsen diffusion transport mechanism in general rather low and to a first approximation proportional to the square root out of the molecular weight ratios of the different components. Significantly higher selectivities can be obtained with homogeneous membranes, where the transport mechanism is based on the solution and diffusion of the various components within the membrane phase. The mass transport in a so-called solution-diffusion membrane has been discussed earlier and is illustrated in Figure 2.15. It consists of three relevant steps:

1. Sorption of the various components from a feed mixture according to their partition coefficient between the gas and polymer phase;
2. diffusion of the individual components within the membrane phase according to their activity gradients;
3. desorption of the components from the membrane into the permeate.

The driving force for the mass transport of gases in solution-diffusion type membranes is the activity gradient of the permeating components within the membrane phase which can be related to the components partial pressures in the feed mixture and in the permeate. According to equations (2.190) to (2.196), the flux of a component in gas separation in a membrane without viscous flow and no coupling of fluxes is given by:

\[
J_k = -D_k^m \frac{\dot{P}_k \phi_k^f - \dot{P}_k \phi_k^i}{\Delta z} = -P_k \frac{\phi_k^m \phi_k^f - \phi_k^m \phi_k^i}{\Delta z}
\]  

(6.21)

Here (') and (") refer to the feed mixture and the permeate, respectively, \(J_k\), \(D_k^m\), \(P_k\), \(\phi_k\), \(\phi_k^f\), \(\phi_k^i\) and \(\Delta z\) is the thickness of the membrane.
The product of diffusion and partition coefficient is the permeability coefficient.

\[ P_k = D_k^m k_k \]  

(6.22)

In deriving Equation (6.21) for the mass transport in solution-diffusion membranes it is assumed that, the sorption and desorption is fast compared to the diffusion in the membrane and that equilibrium is achieved at the interfaces. It should also be noted that the diffusion coefficient and the solubility coefficient are functions of the temperature and the concentrations of the components in the membrane. Especially in permeation of organic vapors, the diffusion coefficient may vary by several orders of magnitude with the concentration of the permeating components.

It should be pointed out that it is generally not possible in gas and especially vapor permeation to predict the mass transport behavior of various components in a mixture from single component measurements.

For a practical application the separation efficiency of the membrane is a crucial parameter. In gas permeation the separation efficiency of a membrane is expressed by its selectivity. The selectivity of a membrane for various components of a mixture is defined by the ratio of the permeabilities. For a binary mixture with the components i and j, the selectivity is:

\[ S_{j,k} = \frac{P_j}{P_k} \]  

(6.23)

Here, \( S_{j,k} \) is the permeation selectivity of a membrane for the components i and k, and \( P_k \) and \( P_j \) are their permeabilities.

The permeation selectivity can be split into two terms:

\[ S_{j,k}^p = S_{j,k}^D S_{j,k}^k \]  

(6.24)

Here, \( S_{j,k}^D \) and \( S_{j,k}^k \) are the diffusivity and solubility selectivity, respectively, of a membrane for the components k and j.

The selectivity is a useful parameter to characterize a membrane. For the design of a membrane plant, however, the separation factor and the enrichment factor are more useful. For a binary mixture the separation factor is defined by:
\[ \alpha_{jk} = \frac{X'_j X'_k}{X'_j X'_k} \]  

(6.25)

Here \( \alpha \) is the separation factor and \( X \) is the mole fraction, the subscripts \( k \) and \( j \) refer to the two components, and the superscripts (') and (") refer to the feed and the permeate.

The separation factor is defined to be always \( > 1 \). It is related to the membrane selectivity by:

\[ \alpha_{jk} = S_{j,k} \frac{X'_j \phi'_j p'_j}{X'_k \phi'_k p'_k} - X'_k \frac{\phi'_j}{\phi'_k} \frac{X'_j}{X'_k} \]  

(6.26)

Here \( \alpha \) is the separation factor, \( S \) is the membrane selectivity for a binary mixture, \( p \) is the pressure and the partial pressure, respectively, \( \phi \) is the fugacity coefficient and \( X \) is the mole fraction. The superscripts (') and (") refer to the feed and the permeate, and the subscripts \( k \) and \( j \) to the components in the mixture.

For an infinitely small ratio of permeate to feed pressure, i.e., \( \lim p''/p' \to 0 \), the separation factor becomes identical with the selectivity times the ratio of the fugacity coefficients in the feed mixture:

\[ \alpha_{jk} = S_{j,k} \frac{\phi'_j}{\phi'_k} \]  

(6.27)

Equations (6.26) and (6.27) indicate that the highest separation factor is obtained when the ratio of feed side to permeate side pressure is at maximum. Then the separation factor \( \alpha \) approaches the selectivity of the membrane. In praxis this can be achieved by operating either with a vacuum on the permeate side or using high pressure on the feed side. The flux through a membrane is proportional to the pressure difference between the feed and the permeate side as indicated in Equation (6.21). This means to obtain high fluxes the pressure difference between feed and permeate should be as high as possible and the obtain high separation the pressure ratio between the feed and permeate should be as high as possible.

For practical applications the enrichment factor \( \beta \) is also used in addition to the separation factor \( \alpha \). \( \beta \) is usually expressed by the ratio of the mole fractions \( X_i \) of the more permeable component in the permeate to that in the feed:
\[ \beta_j = \frac{X_j'}{X_j} \]  

(6.28)

The conversion of \( \alpha \) in \( \beta \) and vice versa is given by:

\[ \beta_j = \frac{\alpha_{j,k}}{1 + (\alpha_{j,k} - 1)X_j} \]  

(6.29)

In vapor separation both \( \alpha \) and \( \beta \) are normally functions of the feed concentration.

It should further be noted that the separation factor \( \alpha \) may be expressed by either the mole fraction \( X \) or the weight fraction \( w \) resulting in the same numerical value for \( \alpha \). The enrichment factor \( \beta \) expressed by the weight fraction \( w \) is different from \( \beta \) expressed by the mole fraction.

For a practical application of gas permeation, a feed stream of a given composition enters a membrane module. Under the driving force of a hydrostatic pressure difference some component permeate the membrane and the feed stream is split into a permeate and a retentate stream. If the membrane has a higher permeability for one of the components in the mixture than for others the component will be enriched in the permeate and the retentate will be depleted of this component accordingly. For practical purposes, it is of interest:

1) how far a given mixture can be depleted of a certain component;
2) how much can a given component be enriched in the permeate;
3) how much of the original feed stream can be recovered as permeate or retentate;
4) how much membrane area is required for this operation.

The process is schematically shown in Figure 6.7.

Fig. 7 Schematic diagram illustrating the gas separation process as unit operation
The process illustrated in Figure  can be described by the following mass balance:

\[ Q_o X_k^o = Q_p X_k^p + Q_r X_k^r \]  

Here \( Q \), the volume fluxes and \( X \) is the mole fraction, the subscripts \( o, p, r \) and \( k \) refer to the feed, the permeate, the retentate, and the component \( k \) respectively, the superscripts of the molefraction refer to the feed, the permeate and the retentate, respectively.

The composition of the retentate and the permeate can be expressed as a function of stage-cut, i.e. the amount of the feed that has been obtained as permeate or retentate respectively. The stage-cut is corresponding with the recovery rate used in ultrafiltration and reverse osmosis and is given by:

\[ \theta = \frac{Q_p}{Q_o} \]  

In gas permeation, the achievable separation, i.e. the enrichment of a certain component in the permeate or its depletion in the retentate, depends on:

1. membrane parameters such as its selectivity and permeability;
2. operational variables such as pressures in the feed and the permeate and the stage-cut; and
3. the flow pattern of the gas streams on the feed and permeate sides of the membrane.

The flow pattern depends, in turn, on the geometry of membrane module design. In gas separating systems three idealized flow patterns may be assumed. These flow patterns are illustrated in the schematic drawing of Figure 6.8.

The determination of the membrane area requirement and separation characteristics for the different flow patterns for binary and multicomponent mixture, are described in the literature and computer program for parametric studies are available for all flow patterns.

The effect of the various flow patterns on the performance of a unit is rather significant, as schematically indicated in Figure 6.9. Here the separation of oxygen and nitrogen is used as an example. The mole fraction of oxygen in the permeate and the retentate is shown as a function of the stage cut for a membrane having a selectivity of 2 of oxygen over nitrogen. The pressure ratio \( p''/p' \) is assumed to be < 0.01.
6.2.3. The permeation cascade

The separation obtained in a single permeation stage can be multiplied many times, if necessary, by connecting an appropriate number of stages in series to form a countercurrent permeation cascade. There are two possible arrangements. In the first arrangement there is no reflux of the retentate. A typical section of a permeation cascade without reflux of the retentate is shown in Figure 6.10 a).

Fig. 6.8  Schematic diagram illustrating four idealized feed and permeate flow pattern used in gas separation systems. a) Complete mixing of feed and permeate; b) co-current plug flow of feed and permeate; and c) counter-current plug flow of feed and permeate.
Fig. 6.9. Mole fraction of oxygen (—) and nitrogen (———) in the permeate and the retentate separate from air with a membrane having a selectivity of 2, a feed to permeate pressure ratio of 100 and a oxygen mol fraction in the feed of 0.2 calculated for a system with a) complete mixing, b) co-current, and c) counter-current flow.

In this simple arrangement the permeate from stage \( n \) becomes the feed for the next higher stage \( n + 1 \) and the retentate is disposed of. In the second case the retentate is refluxed, i.e the
retentate of stage n is mixed with the next lower stage n -1 and so on. All permeate streams must be recompressed before entering a higher stage. The simple cascade without reflux of the retentate is only of use when the retentate is virtually of no value and large enrichment factors or the product in the permeate is required. If a cascade with reflux of the retentate is used there are two sections depending on the position where the original feed solution is introduced into the cascade. One is the so-called enrichment section where the product is enriched in the permeate and the stripping section where the product is enriched in the retentate. The principle of a permeation cascade is illustrated in Figure 6.10 b), which the flow diagram of a cascade with reflux of the retentate.

Fig. 6.10. Flow diagram of permeation cascades a) without reflux of the retentate and b) with reflux of the retentate.

The number of stages required for a required separation factor can be determined by the McCabe-Thiele method, a graphical procedure commonly used in the design of distillation columns. The subject of cascade operation is of rather fundamental importance for all separation processes and therefore treated in detail in the corresponding literature.
The graphical procedure of determining the number of stages is based on two basic relations. One is the equilibrium curve expressing the relation between the composition of the permeate and the retentate in one stage, this is a function of the membrane properties, operating pressures, stage cut, and flow pattern. The second curve is the operating line which describes the relation between the composition of the permeate leaving the n's stage and that of the retentate of the next higher stage, n-1. The operating line depends on the operating scheme used in a cascade, e.g., variable or constant stage-cut, and is the material balance between two stages. The consequent application of the countercurrent flow principle in a reflux cascade has led to the development of the membrane column by Hwang and his co-workers. In analogy to distillation a membrane column can be regarded as a reflux cascade with an infinite number of stages and like a reflux cascade the membrane column will produce an enriched retentate in the stripping section and an enriched permeate in the enrichment section. Compared to the normal cascade the membrane column has the advantage of being able to produce highly enriched products both in the permeate and retentate without pressurizing the permeate before going into the next stage of the cascade, thus requiring less energy for the compression of the gas. On the other hand the membrane column requires a significantly higher membrane surface area. Which principle - column or cascade - will be optimal for a given separation problem must be decided by an economic analysis. It is highly depending on membrane properties and module design. Although the membrane column concept can in principle be applied to other membrane separation processes such as reverse osmosis, it is most important for gas separation.

6.2.3 Pervaporation

In pervaporation volatile organic components are removed from a liquid feed mixture through a semipermeable membrane into a gas phase as illustrated in Figure 6.11, which shows schematically the operating principle of pervaporation.
Thus pervaporation is a membrane process which combines the evaporation of volatile components with their permeation through a selective membrane. The transport of a component through a pervaporation membrane consists of three consecutive steps:

1. Sorption of the component from the liquid feed into the membrane material,
2. diffusion of the dissolved component through the membrane matrix.
3. desorption of the component from the membrane into the vapor phase.

The separation of various components from a liquid mixture is not only determined by differences in their vapor pressure but also by their permeation rate through the membrane. The actual driving force for the permeation of the different components through the membrane is their chemical potential difference between the two phases separated by the membrane. The chemical potential difference between the two phases is inducing a concentration gradient within the membrane interphase as indicated in Figure 6.12. In pervaporation the chemical potential gradient is usually induced by either applying a vacuum on the permeat side of a membrane or by using a sweep gas to remove the permeating component and by applying a temperature difference between the liquid feed mixture and permeat gas phase.
Fig. 6.12 Mass transport through a solution diffusion membrane in pervaporation

All three procedures referred to as (1) vacuum, (2) sweep gas, and (3) temperature pervaporation, lead the build up of a partial pressure difference of the components in the two phases separated by the membrane and are used to remove organic volatile components from a liquid mixture. The sweep gas and vacuum operation mode are shown schematically in Figure 6.13.

Fig. 6.13 Schematic drawing illustrating a) vacuum and b) sweep gas pervaporation operation mode
Mathematically the mass transport in pervaporation can be described by Equation (2.179) derived from the general phenomenological relation of mass transport in the previous section of this outline. The flux of a component i can then be expressed by:

\[ J_i = -D_i^m k_i \frac{p_i^{'} \phi_i - X_{i, p}^o \phi_i}{\Delta z} = \frac{p_i^{'} \phi_i - X_{i, p}^o \phi_i}{\Delta z} \]  

(6.32)

Here J is the molar flux, D is the diffusion coefficient, k is the partition coefficient of the components between the membrane and the outer phases, P is the permeability coefficient, p is the pressure the partial pressure, ϕ the fugacity coefficient, X the mole fraction, γ the activity coefficient, and Δz the thickness of the membrane; the superscripts (′), (′′), refer to the feed and the permeate, the subscripts i refers to a component.

Equation (6.32) describes the permeation flux of a component i as a function of the feed and permeate mixture composition and its diffusivity and solubility in the membrane which can easily be determined by independent measurements. The practical application of Equation (6.32), however, is rather limited since the diffusion coefficient as well as the partition coefficient are not constant but depend strongly on the concentration of the permeating component in the outside phases. This dependency must be determined experimentally and may be different for different membrane materials and vapors.

The selectivity of the membrane is given by:

\[ S_{ij} = \frac{P_i}{P_j} \]  

(6.33)

Here P is the permeability of the membrane, S is the membrane selectivity, and i and j refer to the components of the mixture.

The separation factor which for a mixture consisting of two components is given by:

\[ \alpha_{i,j} = S_{i,j} \frac{X_i^o \phi_i^o P - X_i^o p^o}{X_j^o \phi_j^o P - X_j^o p^o} \frac{X_j}{X_i} \]  

(6.34)

Here \( \alpha \) is the separation factor, S the membrane selectivity, X the molar fraction, p the pressure, γ the activity and ϕ the fugacity coefficient, the subscripts i and j refer to components of the mixture, and the superscripts o, (′) and (′′) refer to saturation pressure, feed and permeate, respectively.
In pervaporation the partial pressure of the components on the permeate side is kept as low as possible by either using a sweeping gas or more commonly applying a vacuum. For a pervaporation experiment using a vacuum the separation factor is to a first approximation given by:

$$\alpha_{ij} = S_{ij} \frac{\gamma_i^o p_i^o}{\gamma_j^o p_j^o}, \quad \lim p'' = 0 \quad (6.35)$$

It should be noticed that the separation factor consists of two terms the first term, i.e. $S_{ij}$ represents the membrane selectivity which is determined by the membrane and the permeating components and the second term $\frac{\gamma_i^o p_i^o}{\gamma_j^o p_j^o}$ the thermodynamic liquid/vapor equilibrium which represents the separation that would be achieved by distillation. In pervaporation the membrane selectivity can increasing or decrease the distillation selectivity and eventually pushing the overall separation factor into the opposite direction.

The evaporation selectivity is usually expressed by the so-called McCabe-Tiele-diagram, in which the composition of a mixture in the vapor phase is shown as a function of the composition in the liquid phase. The same can be done for the the pervaporation selectivity as shown in Figure 6.14

Fig. 6.14  Vapor-liquid equilibrium of a water methanol mixture obtained by distillation and pervaporation with a PDMS- and a PVA-membrane
6.2.4. Concentration gradient driven membrane separation processes

The mass transport through the membranes of the living cells occurs in most cases under isobaric and isothermic conditions with a concentration gradient being the only driving force. It seems, therefore, quite obvious that dialysis was also the first technically used membrane separation process and is still today amongst the commercially most significant ones since more than 80% of today's artificial kidneys are dialyzers. With the production of more than 50 million dialyzers per year, hemodialysis is the largest single application of a membrane separation process.

A dialyzer is a device in which one or more solutes are transferred from one solution to another through a membrane under the driving force of a concentration gradient. The solution to be depleted of a solute is called the feed and the fluid receiving the solute is referred to as dialysate. The operating principle of a dialyzer is illustrated in Figure 6.15, which shows a cell separated by a membrane into two chambers.

![Operating principle of a dialyzer](image)

A feed solution to be depleted of a solute is pumped through one chamber while the receiving fluid, i.e. the dialysate, is passed through the other chamber. The overall efficiency of a dialyzer is governed by two interdependent factors: the ratio of the flow rates of the two fluids; and the rate constant for solute transport between the fluids (which is determined by the properties of the
membrane, the membrane area, the fluid channel geometry, and the local fluid velocities). With reference to Figure 6.15, a material balance can be expressed as:

\[ Q^i \left( C_{sf}^i - C_{sd}^i \right) = Q^d \left( C_{sd}^i - C_{sf}^o \right) \]  

(6.36)

Here \( Q \) is the volumetric flow rate; \( C \) is the solute concentration, subscripts \( s, f \) and \( d \) refer to solute, feed and dialysate, respectively, superscripts \( i \) and \( o \) designate inlet and outlet conditions, respectively.

The overall rate of solute transport from the feed to the dialysate can is be expressed by

\[ J_s = Q^i \left( C_{sf}^i - C_{sf}^o \right) = Q^d \left( C_{sd}^i - C_{sd}^o \right) \]  

(6.37)

The solute transfer \( J_s \) can also be expressed by:

\[ J_s = k_d A \Delta C_s \]  

(6.38)

where \( \Delta C_s \) is the average solute concentration difference between the fluids, \( A \) is the membrane area, and \( k_d \) is the overall rate constant. The proper average solute concentration difference used is the logarithmic mean of the inlet and outlet differences. The three most common cases to be considered are parallel flow of both fluids, countercurrent flow, and flow with the dialysate completely mixed.

The efficiency of a dialyzer is expressed in terms of its "dialysance" \( D_f \), which is defined as:

\[ D_f = \frac{J_s}{C_{sf}^i - C_{sd}^i} \]  

(6.39)

The dimensionless ratio \( \frac{D_f}{Q_f} \) can be regarded as a efficiency parameter, since it represents the fraction of maximum attainable solute depletion in the feed that is actually achieved in the device.

By simultaneous solution of Equations (6.37), (6.38) and (3.39) and the use of the logarithmic mean concentration difference driving force, the dialysance ratio \( \frac{D_f}{Q_f} \) can be expressed as follows:
1) Parallel flow:

\[
\frac{D_L}{Q_t} = \frac{1}{1+z} \left(1 - e^{-y(l+z)}\right)
\]  

(6.40)

2) Mixed-dialysate flow:

\[
\frac{D_L}{Q_t} = \frac{1 - e^{-y}}{1 + z(1 - e^{-y})}
\]  

(6.41)

3) Countercurrent flow:

\[
\frac{D_L}{Q_t} = \frac{1 - e^{-y(l-z)}}{z - e^{-y(l-z)}}
\]  

(6.42)

where \( z = \frac{Q_z}{Q_d} \) and \( y = k_d \frac{A}{Q_f} \).

The above relationships can be used to analyze dialyzer performance and to calculate expected performance for different flow rates.

The overall rate constant \( k_d \) is influenced by the properties of the membrane and of the fluid boundary layers on each side of the membrane. These factors are discussed in detail in the literature describing the artificial kidney and will not be covered here.

6.2.5 Electrodialytic membrane processes

Electrodialytic processes include electrodialysis, Donnan dialysis, diffusion dialysis, and the electrodialytic water dissociation with bipolar membranes. Of technical importance are today only electrodialysis while the other processes are still in a laboratory or pilot plant stage.

6.2.5.1 Electrodialysis

The performance of electrodialysis in practical applications is not only a function of membrane properties and feed solution composition. It is also determined by several process and equipment design parameters such as electrodialysis stack construction, i.e. the cell geometry and the spacer configuration, the feed flow velocities, and mode of operation, i.e. continuous or batch operation with co- or counter-current flow streams. These parameters effect the cost of the process directly by determining the investment costs, and indirectly by effecting the limiting current density, the voltage drop, the hydraulic pressure losses and the current utilization.

The basic concept of electrodialysis has been discussed earlier and is shown in Figure 2.8 This figure depicts the transport of ionic species in a cell arrangement consisting of cation- and anion-exchange membranes in alternating series forming an array of individual cells between two
electrodes. A device in which the cells are "stacked" with electrodes on both ends is referred to as an electrodialysis stack. For designing and operating an electrodialysis stack certain process parameters have to be taken into account and controlled such as the feed solution concentration and the desired product and brine concentrations. Various modes of operation are possible such as batch type or continuous. The flow streams through a stack can be counter- or co-current. The velocities of the flow streams will effect the concentration polarization and thus the limiting current density which determines the required membrane area for a given capacity desalination plant. The flow velocities, on the other hand, determine the degree of desalination and concentration that can be achieved in one pass in a stack of a given geometry and the pressure. Certain process parameters are fixed by the feed and product solution properties. Other parameters may be varied in a certain range and can thus be utilized to optimize the process, such as the current density, the applied voltage, the flow stream velocities, etc. Many parameters are interdependent and often counteracting in terms of overall process efficiency. Before describing the different hardware components and the process scheme in more detail some basic relations concerning the flow streams, the rate of desalination, concentration polarization effects, etc. shall be discussed.

6.2.5.1.1 Material balance between the diluate and concentrate flow stream
To remove a certain amount of salt from a feed solution of a given concentration it is fed into an electrodialytic cell arrangement which must contain at least two compartments, and two membranes, i.e. a cation- and an anion-exchange membrane, between two electrodes as indicated in Figure 6.16. This two compartments, two membranes arrangement is referred to as a cell pair.
Fig. 6.16 Schematic drawing illustrating the ion transfer in an electrodialysis cell pair due to migration in direction perpendicular to the membrane surfaces and convection parallel to the membrane surface.

Due to an applied electrical potential ions are removed from one compartment which is referred to the diluate cell and concentrated in the other, i.e. the concentrate cell. The degree of desalination can be expressed by a material balance between the feed, the concentrate and the diluate solutions. It is a function of the residence time of the different solutions in the cells, i.e. the flow velocities of the solutions and the applied current density. It is given by the concentration difference between the feed and the product and the feed and the concentrate. The concentration differences can be related to the current passing through the cell. It is given by:

\[
\left( \frac{\text{in}_{C_s}^{d} - \text{out}_{C_s}^{d}}{\text{dt}} \right) \frac{dV_d}{dV_c} = \left( \frac{\text{out}_{C_s}^{c} - \text{in}_{C_s}^{c}}{\text{dt}} \right) \frac{dV_c}{dV_c} = \frac{\xi I}{\nu_z F} \quad (6.43)
\]

Here C is the salt concentration, \( \xi \) is the current utilization, I is the total current passing through the cell pair, \( z \) the valence, \( \nu \) the stoichiometric coefficient, F the Faraday coefficient and \( \frac{dV_d}{dV_c} = Q \) is the flow velocity of the solutions in the cells parallel to the membrane surface. The superscripts in and out refer to the inlet and the outlet of an cell area element, c and d refer to
concentrate and diluate; the subscripts s and c refer to salt solution and cations. The current utilization gives the portion of the current passing through an electrodialysis stack that is used for the transport of ions. It is a function of the membrane properties and the cell design. In practical applications the current utilization is always close to 1.

The salt concentration in both the diluate and the concentrate streams changes from the cell entrance to the cell exit. Therefore, the resistance of the solutions and at constant voltage the current density is also changing. The concentration change in diluate and the concentrate streams while it is passing through the cell are given by:

\[
\begin{align*}
\frac{dC_s^d}{dA} &= \frac{\xi i}{z_c \nu_c F Q d} \text{ and } \\
\frac{dC_s^c}{dA} &= \frac{\xi i}{z_c \nu_c F Q c}
\end{align*}
\] (6.44)

Here \(Q^d\) and \(Q^c\) are the diluate and concentrate flow velocities in the cells, \(i\) is the current density, \(dA\) is a cell area element which is given by the cell width \(Y\) and \(dx\) a distance in direction of the flow stream parallel to the membrane surface as depicted in Figure 6.16. Thus \(dA = Y dx\).

The current density in a cell pair for an electrolyte solution containing a monovalent single salt, i.e. \(z\) and \(\nu\) are unity, is given to a first approximation by:

\[
i = \frac{U}{\Lambda_s C_s^d + \frac{\Delta^d}{\Lambda_s C_s^d} r^a m + r^c m + \frac{\Delta^c}{\Lambda_s C_s^c}}
\] (6.44)

Here \(U\) is the applied voltage across the cell pair, \(\Delta^d\) is the thickness of the diluate and \(\Delta^c\) that of the concentrate cell, \(\Lambda_s\) is the equivalent conductivity, \(r^a m\) and \(r^c m\) are the resistance's of the anion- and cation-exchange membranes; \(C_s^d\) and \(C_s^c\) are the concentration of the diluate and the concentrate, respectively.

In most electrodialysis stacks the diluate and concentrate cells have the same geometry and the flow velocities of diluate and concentrate are kept equal, i.e. \(\Delta^d = \Delta^c = \Delta\) and \(Q^d = Q^c = Q\) and the voltage drop across the cell pair is constant over the entire cell length. Under these assumption the change in the salt concentration in the diluate and concentrate in the area element is given by combining Equations (6.43) and (6.44)
\[
\frac{dC_s^d}{dt} = \frac{U}{\Lambda_s(C_s^c + C_s^d) + r^am + r^cm} \int_0^x \xi Ydx \tag{6.45}
\]

The rate of the salt transfer between the cell entrance to the cell exit is given by the mass balance applied to the salt:

\[
\left(\frac{\text{out } C_s^c - \text{in } C_s^c}{\text{dt}}\right) = \left(\frac{\text{in } C_s^d - \text{out } C_s^d}{\text{dt}}\right) = \frac{dC_s}{dt} \tag{6.46}
\]

The change in concentration of the diluate and concentrate solutions from the entrance to the exit of the cell is obtained by integration over the cell length.

Rearranging Equation (6.46) and introducing Equation (6.45) with the assumption that volume flows in the concentrate and diluate cells are equal, i.e. \(\frac{dV^c}{dt} = \frac{dV^d}{dt} = Q\) leads to:

\[
\frac{dC_s}{\left(\frac{\text{in } C_s^d - C_s}{\text{in } C_s^c + C_s}\right) + dC_s} + \Lambda_s \left(\frac{r^am + r^cm}{\Delta}\right) \left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right) = \frac{\Lambda_s \xi YX FQ}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} \tag{6.47}
\]

Integration with the boundary conditions that at the cell entrance \(x = 0\) and \(C_s = 0\) and at the cell outlet \(x = X\) and \(C_s = C_s\) leads to:

\[
-\frac{1}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} \ln \frac{\text{in } C_s^d - C_s}{\text{in } C_s^c + C_s} + \frac{1}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} \ln \frac{\text{in } C_s^d - C_s}{\text{in } C_s^c + C_s} + \frac{\Lambda_s \left(\frac{r^am + r^cm}{\Delta}\right)}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} = \frac{\Lambda_s \xi YX FQ}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} \tag{6.48}
\]

Rearrangement of Equation (6.48) leads to a relation for the product and brine concentration in electrodialysis as a function of various stack design and operating parameters:

\[
\ln \frac{\text{out } C_s^c \text{in } C_s^d}{\text{out } C_s^d \text{in } C_s^c} + \frac{\Lambda_s \left(\frac{r^am + r^cm}{\Delta}\right)}{\left(\frac{\text{in } C_s^c}{\text{in } C_s^c + \text{in } C_s^d}\right)} = \frac{\Lambda_s \xi YX FQ}{\text{Q}} \tag{6.49}
\]

Here \(\text{in } C_s^d\) and \(\text{in } C_s^c\) are the concentrations of the diluate and the concentrate at the cell inlet, \(\text{out } C_s^d\) and \(\text{out } C_s^c\) are the concentrations of the diluate and the concentrate at the cell outlet, \(\Lambda_s\) is equivalent conductivity of the salt solution, \(r^am\) and \(r^cm\) are the area resistance's of the anion-
and cation-exchange membrane, Λ is the cell thickness, i.e. the distance between the cation- and anion-exchange membrane, Q is the flow velocity of the diluate and concentrate stream, respectively, U is the voltage drop across a cell pair, ξ is the current utilization, F the Faraday constant, Y and X are the width and the length of a cell, i.e. Y x Y = A_{cell} the area of the cation- or anion-exchange membrane in the cell.

Equation (6.49) shows that for given feed solution, membrane properties, flow velocity, cell geometry and voltage drop the concentration of the brine and the diluate is an exponential function of the cell length. It can be considered as a basis for designing and operating an electrodialysis stack.

Effect of process design on concentration polarization and limiting current density

In electrodialysis one consequence of concentration polarization is the depletion of ions in the laminar boundary layer at the membrane surface in the diluate solution which leads to a limiting current density. In a practical application of electrodialysis the limiting current density should not be exceeded. The causes for the limiting current density and their consequences have been discussed earlier. The relation between the limiting current density and various process parameters such as membrane properties, diluate concentration, etc. for a cation-exchange membrane given by:

\[ i_{\text{lim}} = -\frac{F D_s}{\xi_c \left( T^m_c - T_c \right)} \left( \frac{b C^d_s}{\Delta z} \right) \]  

(6.50)

Here \( i_{\text{lim}} \) is the limiting current density, F is the Faraday constant, D is the diffusion coefficient, C is the concentration, T is the transport number, and \( \Delta z \) is the laminar boundary layer at the surface of the membrane which faces the diluate solution; the superscripts m, b, and d refer to the membrane, the boundary layer at the membrane surface and the diluate, respectively; the subscript s and c refer to salt and cation.

The boundary layer \( \Delta z \) is a function of the hydrodynamics of the feed solution, i.e. the flow velocities, the cell geometry, the spacer design, etc. The other parameters, which determine the limiting current density, are the diluate concentration, the salt diffusion coefficient and the transference numbers of the ions in the membranes. For economic reasons, however, it is desirable to operate an electrodialysis unit at as high as possible current densities.

The hydrodynamic situation in an electrodialysis cell is generally quite complex and it is very difficult to calculate the mass transfer in the boundary layer. In practical processes an empirically derived expression is used which describes the limiting current density as a function to the feed flow velocity in the electrodialysis stack by:
Here \( b_{cs}^d \) is the concentration of the solution in the bulk of the diluate cell, \( u \) is the linear flow velocity of the solution through the cells parallel to the membrane surface and \( a \) and \( b \) are characteristic constants for a given stack design and must be determined experimentally. This is done in practice by measuring the limiting current density in a given stack configuration and constant feed solution salt concentrations as a function of the feed flow velocity.

The limiting current density can be determined by measuring the current as a function of the applied voltage across a cell pair. Result of this type of measurements are shown in Figure (6.17) which shows the current density measured with a cation-exchange membrane (CMX of Tokuyama Soda) in a 0.05 molar NaCl-solution. The slope of the curve is inverse proportional to the electrical resistance of a cell.

![Graph](image)

**Fig. 6.17** Experimentally determined current versus voltage curve measured with a cation-exchange membrane (CMX of Tokuyama Soda) in a 0.05 molar NaCl-solution.

When the limiting current density is reached the electric resistance of the cell is increasing drastically and the current density increases very little with increasing voltage until the so-called over-limiting current density is reached and the current increases further due to water dissociation and electro-convection effects (Krol et al. 1998). The limiting current density is determined by the intersection of the first and the second slope of the curve.

Another method of determining the limiting current density is suggested by Cowan and Brown by plotting the overall resistance versus the reciprocal current density as shown schematically in Figure 6.18 (Cowan and Brown 1959). The curve goes through a sharp change in the resistance.
which corresponds to an incipient sharp change in the pH-value of the diluate solution as also shown in Figure 6.18. The pH-drop in the diluate cell is due to that water dissociation at the anion-exchange membrane.

Fig. 6.18 Schematic drawing illustrating the determination of the limiting current density from a plot of the electrical resistance and the pH-value of the diluate solution as a function of the reciprocal current

Membrane Fouling and Poisoning
Suspended and colloidal matter, polyelectrolytes, organic anions and multivalent salts near the saturation level can cause severe problems in electrodialysis due to precipitation on the membrane surfaces or by partial penetration into the membranes. Precipitation of suspended matter, silicates and salts with low solubility such as calcium carbonates or iron hydroxides may occur within the actual flow channels resulting in high hydrodynamic pressure losses and non-uniform flow distribution in the stack. Precipitation on the surfaces of the membranes also causes an increase the electrical resistance of the stack and may lead to physical damage of the membranes. Especially organic anions such as humates can precipitate on the anion-exchange membranes as humic acid and cause a sharp increase in the electric resistance. Mechanical cleaning and treatment with a dilute bases and acids can generally restore the original properties of the membranes. More severe is the poisoning of membranes by organic anions that are small enough to penetrate the membranes but whose mobility in the membrane is so low that they virtually remain inside the membrane causing a drastic increase in the membrane resistance. Certain detergents are also the cause of this type of poisoning which is very difficult to deal with and can best be avoided by a proper pre-treatment of the feed solution.

The various pretreatment procedures such as precipitation, flocculation or ion-exchange and rinsing cycles can be substantially reduced by a simple but very effective operating mode which is referred to as electrodialysis reversal. In the electrodialysis reversal operating mode, which has
been developed by Ionics Incorporated (Ionics 1965), the polarity of the electric field applied to the electrodialysis stack as the driving force for the transport of ions is reversed in certain time intervals. Simultaneously the flow streams are reversed, i.e. the diluate cell becomes the concentrate cell and vice versa with the result that matter that has been precipitated at the membrane surface will be redisolved and removed with the flow stream passing through the cell. The principle the electrodialysis reversal operating mode is illustrated in Figure 6.19.

![Image of electrodialysis reversal operating mode](image)

**Fig. 6.19** Schematic drawing illustrating the removal of deposited negatively charged colloidal components from the surface of an anion-exchange membrane by reversing the electric field

This figure shows a typical electrodialysis cell formed by a cation- and anion-exchange membrane between two electrodes. If an electric field is applied to a feed solution containing, e.g. negatively charged particles or large organic anions these components will migrate to the anion exchange membrane and be deposited on its surface. If the polarity is reversed the negatively charged components will now migrate away from the anion-exchange membrane back into the feed stream and the membrane properties are restored. This procedure has been very effective not only for the removal of precipitated colloidal materials but also for removing precipitated inorganic salts and is used today in almost all electrodialysis water desalination systems.

*The electrodialysis stack design*

A key component in electrodialysis is the membrane stack. The name relates to the fact that in an electrodialysis unit a series of membranes and spacers are stacked between two electrodes. A proper electrodialysis stack design should provide a maximum effective membrane area per unit stack volume. The cell and spacer screen design should ensure equal and uniform flow distribution in each compartment. Any leakage between the diluate, concentrate and the
electrode cells should be prevented. The spacer screen should provide a maximum of mixing of the solutions at the membrane surfaces and should cause a minimum in pressure loss. In praxis two different stack types are used on a large scale. One is the so-called sheet-flow and the other the tortuous path-flow stack.

A typical sheet-flow electrodialysis stack is shown in Figure 6.20. It is a device to hold an array of membranes between electrodes in such a way that the flow streams are kept separated. Gaskets around the perimeter of the cell confine the solutions within a compartment formed by two membranes. But the gaskets not only separate and seal the membranes but also contain manifolds to distribute the process fluids in the different compartments. The supply ducts for the diluate and the brine are formed by matching holes in the gaskets, the membranes and the electrode cells. The solution flow is approximately in a straight path from the entrance to the exit ports, which are located on opposite sides in the gasket.

![Schematic drawing of a sheet flow electrodialysis stack](image)

Fig. 6.20 Schematic drawing of a sheet flow electrodialysis stack

The distance between the membrane sheets, i.e., the cell thickness, is typically between 0.5 to 2 mm. A spacer is introduced between the individual membrane sheets to support the membrane and to help to control the feed solution flow distribution. A sheet-flow spacer gasket with the manifolds for the distribution of the flow streams is shown in Figure 6.20. The most serious design problem for an electrodialysis stack is that of assuring uniform flow distribution in the various compartments and good mixing of the solutions in the cell at low pressure losses. Different types of spacer screens have been studied for their use in a sheet-flow stack. Two of them are
mainly used today. One is a woven and the other a non-woven netting as also indicated in Figure 6.21. The main difference between the non-woven and the woven spacer is the pressure loss when the solutions are pumped through the stack. The non-woven spacer has a significantly lower pressure loss than a woven spacer of comparable mesh size and flow distribution. In a practical electrodialysis system, 200 to 1,000 cation- and anion-exchange membranes are installed in parallel to form an electrodialysis stack with 100 to 500 cell pairs. At each end of a stack there is an end-plate that contains the electrodes and the connections that rinses the electrodes.

Fig. 6.21 Concept of a sheet-flow electrodialysis spacer gasket and the two different types of screens a) non-woven and b) woven used in commercial stacks

A variation of the sheet flow spacer is the so-called tortuous-path spacer. Here the spacer and gasket have a long serpentine cut-out which defines a long narrow channel for the fluid path. The
objective is to provide a long residence time for the solution in each cell in spite of a high linear velocity that is required to limit polarization effects. A tortuous-path spacer gasket is shown schematically in Figure 6.22. Solution flow velocities in sheet-flow stacks are typically 3 to 10 cm s\(^{-1}\), whereas in tortuous-path stacks, solution flow velocities are 15 to 50 cm s\(^{-1}\). Because of higher flow velocities and longer flow paths, higher pressure drops in the order of 2 to 3 bars are obtained in stacks with tortuous-path spacers than in sheet-flow systems where pressure drops are between 0.5 and 2 bars. However, higher velocities help to reduce the deposition of suspended solids such as polyelectrolytes, humic acids, surfactants and biological materials.

Fig.6.22  Schematic drawing illustrating the geometry of a tortuous path spacer

**Electrodialysis process design**

Depending on the feed solution composition and the product requirements electrodialysis unit may be operated in a batch-type, in a continuous or in a feed-and-bleed mode with partial recycle of the diluate and concentrate streams. Independent of the mode of operation their are two basic concepts of using electrodialysis in large-scale applications. The first concept is referred to as the unidirectional electrodialysis and the second as electrodialysis reversal (W.E. Katz 1979). In a unidirectional operated electrodialysis stack an electrical potential gradient is established between the anode and cathode across the stack. The electric field is permanently applied in one direction and the diluate and concentrate cell are also permanently fixed over the period of
operation. A flow diagram of a typical unidirectional operated electrodialysis plant is shown in Figure 6.23.

Fig. 6.23 Flow scheme of an unidirectional operated electrodialysis plant with partial recycling of the diluate and concentrate solutions

After the proper pre-treatment, the feed solution is pumped through the actual electrodialysis unit, which generally consists of one or more stacks in series or parallel. A de-ionized solution and a concentrated brine is obtained. The concentrated and depleted process streams leaving the last stack are collected in storage tanks. To prevent the formation of free chlorine by anodic oxidation, the electrode cells are sometimes rinsed with a separate solution that does not contain chloride. In many cases, however, the feed or brine solution is also used in the electrode cells. Unidirectional-operated electrodialysis plants are rather sensitive to membrane fouling and scaling and often require rinsing of the stack with acid or detergent solutions. The unidirectional
Operating concept is mainly used today for applications in the food and drug industry or in the treatment of certain waste water. In desalination of brackish or surface waters generally electrodialysis reversal is used by which membrane fouling and scaling can be more or less avoided. The process is illustrated in Figure 6.24. In this operating mode, the polarity of the current is changed at specific time intervals ranging from a few minutes to several hours. In the reverse polarity operating mode, the hydraulic flow streams are reversed simultaneously, i.e., the dilute cell will become the brine cell and vice versa. The advantage of the reversed polarity operating mode is that precipitation in the brine cells will be re-dissolved when the brine cell becomes the diluate cell in the reverse operating mode. During the reversing of the polarity and the flow streams, there is a brief period when the concentration of the desalted product exceeds the product quality specification. Thus, a reversal of the flow streams always leads to some loss of product. This is generally no problem in desalination of brackish water. It might, however, be not acceptable in certain applications in the food and drug industry when feed solutions with high value products are processed.

Fig. 6.24 Flow scheme of electrodialysis reversal in a continuous operating mode with the feed solution also used as electrode rinse

Continuous and batch type operation in Electrodialysis
The degree of desalination that can be achieved in passing the feed solution through a stack is a function of the solution concentration the applied current density and the residence time of the solution in the stack. If the flow rates of diluate and concentrate through the stack are relatively
high the degree of desalination or concentration which can be achieved in a single path is quite low and often not sufficient to meet the required product qualities. If this is the case the electrodialysis can either be operated as a batch process, a multistage process, or a process with feed and bleed in which the diluate or the concentrate or both are partially recycled. Most commonly the desired degree of desalination is obtained by staging a required number of stacks. The staging can be done by complete physical separation of the stacks with each having its own set of electrodes, i.e. its own power supply and feed pumps or the required process path length can be achieved by internal staging as illustrated in Figure 6.25.

![Diagram](image)

**Fig. 6.25**  a) Staging of individual stacks with independent power supply and diluate and concentrate pumps, b) internal staging using one pair of electrodes and one pump

In internal staging only one pump and one set of electrodes is needed. The disadvantage of the internal staging is that the total number of stages is limited by the pressure losses of the solution in the stack. These pressure losses can lead to differences in the hydrostatic pressure between the different flow streams with the consequence of leakages between the diluate and the concentrate flow streams. Furthermore, the average current density over the stack is lower in internal staging than the average current density that is obtained when the stages are provided in separated stacks.

A disadvantage of simple staging as was illustrated in Figure is a constant recovery rate fixed at 50% of the feed solution. If variable recovery rates are desired the system must be operated in a feed and bleed mode as illustrated in Figure 6.26.
Fig. 6.26 Flow scheme of an electrodialysis stack operated in a feed and bleed mode, i.e. with partial recycling of the diluate and concentrate solutions

In the feed and bleed mode both the brine and the product concentration can be determined independently and very high recovery rates can be obtained.

Other process variable and their control
Process variables in electrodialysis are feed flow velocities, the applied voltage, the current density, the process path length, or the feed and bleed rates. They can be varied in a certain range taking into account technical feasibility and economic considerations. However, most variables are interdependent. Variations in the flow stream velocities result in shorter residence time of the solutions in the stack with the consequence of lower desalination rates in a single path. On the other hand higher flow velocities result in higher limiting current densities and thus higher desalination rates. To optimize an electrodialysis process for a given feed stream and product requirements in term of overall costs all process variables and their interdependency must be taken into account when designing and operating an electrodialysis plant.

Electrodialysis requires direct current. The voltage necessary to obtain the required current depends on the resistance of a cell pair and the number of cell pairs placed between to electrodes. The inability to alter direct current voltage readily makes it desirable to operate an electrodialysis unit at constant voltage. Since the voltage across the stack is constant and the resistance of the solutions flowing through a stack is changing along the flow path from the entrance to the exit of the cell due the change in concentration in the solutions the current density is also changing along the flow path. In most application the objective in electrodialysis is the production of a product water of a predetermined quality regardless of variations in the feed solution composition or temperature. Constant product water salinity can be achieved by varying the applied voltage and thus the current density in a stack or by adjusting the feed and bleed streams accordingly by changing the recirculation rates of the diluate and concentrate flow streams.
To guarantee an certain capacity and quality of product the electrodialysis unit must be equipped with certain number of monitoring and control devices that are coupled with the power supply and hydraulic system.

In addition to the power supply the hydraulic systems and their control is of importance. For a given stack design the flow velocities of the diluate and concentrate determine the salinities obtained at the stack exit. The flow velocity in the diluate cell determines also the limiting current density. High flow velocities mean high current densities and a high degree of desalination per unit membrane area. High flow velocities cause higher pressure losses in the stack which do not only increase the pumping power consumption, but may cause internal and external leakage.

Many feed solutions in electrodialysis contain suspended and colloidal matter or soluble salts close to their saturation level. These components can caused membrane fouling and poisoning and should be removed in a proper pretreatment of the feed solution.

Before the product water of an electrodialysis unit can be used is potable or industrial process water certain post treatment procedures may be necessary. Since micro-organisms are not removed from a feed stream by electrodialysis most commonly a chlorinating of the product water is required.

Process economics
Process design and economics are closely related in electrodialysis. The total costs are the sum of fixed charges associated with amortization of the plant investment costs and of operating costs, such as energy and maintenance costs. Membrane replacement costs are sometimes regarded as a separate item because of the relatively short life of the membranes. In electrodialysis water desalination the useful life of the membranes is in the order of 5 to 7 years. Other components such as the power supply, the valves, piping, pumps, instrumentation, stack spacers etc. usually last 10 to 20 years.

Investment costs include non-depreciable items such as land and depreciable items such as the electrodialysis stacks, pumps, electrical equipment, monitoring and control devices and membranes. The total investment costs of an electrodialysis plant are a function of the required membrane area which is directly proportional to the plant capacity. For a given plant capacity the required membrane area depends on feed solution and the product water concentration. It is inverse proportional to the current density and direct proportional to the amount of ions removed from a given feed solution. The total current required in electrodialysis for a certain desalination of a feed solution is given by Equation (6.44). Relating the total current to the current density gives the total required membrane area as a function of the plant capacity and the feed and product concentration as shown in the following Equation (6.52):
\[
A_{\text{total}}\bar{i} = NA\bar{i} = I = \frac{Z_i v_i F Q}{\xi} \left( C_s^f - C_s^d \right)
\]

(6.52)

Here \( A_{\text{total}} \) are the total cell pair area and \( A \) the area of one cell pair, \( N \) is the number of cell pairs in a stack, \( I \) is the total current passing through the stack, \( \bar{i} \) the average current density, \( z \) is the valence, \( \nu \) is the stoichiometric coefficient, \( F \) is the Faraday constant, \( Q \) is the product volume flow, and \( C_s^f \) and \( C_s^d \) are the feed concentration and the diluate concentration leaving the stack, i.e. the product concentration.

For an electrodialysis stack operated at constant applied voltage the current density which is given Equation (6.44) should not exceed the limiting current density which is given by Equation (6.50). Thus is:

\[
i = \frac{U_{\text{st}}}{N} \left[ \frac{\Delta^d}{\Lambda_s C_s^d} + \frac{\Delta^c}{\Lambda_s C_s^c} + r^{\text{am}} + r^{\text{cm}} \right] \leq i_{\text{lim}} = \frac{F}{|z_i| \nu_i \left( T_i^m - T_i \right)} \left( \frac{D_s b C_s^d}{\Delta z} \right)
\]

(6.53)

Here is \( U_{\text{st}} \) the voltage drop across the entire stack, \( N \) is the number of cell pairs in the stack, \( \Delta^d \) is the thickness of the diluate and \( \Delta^c \) that of the concentrate cell, \( \Lambda_s \) is the equivalent conductivity, \( r^{\text{am}} \) and \( r^{\text{cm}} \) are the resistance of the anion- and cation-exchange membranes, and \( C_s^d \) and \( C_s^c \) are the concentration of the diluate and the concentrate, respectively; \( i_{\text{lim}} \) is the limiting current density, \( F \) the Faraday constant, \( z \) the valence, \( \nu \) the stoichiometric coefficient, \( D_s \) the salt diffusion coefficient, \( b C_s^d \) the diluate bulk concentration, \( T \) the transport number, \( \Delta z \) the laminar boundary layer at the surface of the membrane which faces the diluate solution, the superscripts \( m, b, \) and \( d \) refer to the membrane, the boundary layer at the membrane surface and the diluate: the subscript \( i \) refer to cat- or anions, respectively.

Assuming, that the diluate and concentrate cells have identical dimensions, i.e. \( \Delta^d = \Delta^c = \Delta \) and that \( b C_s^d = C_s^d \) and introducing a mass transfer coefficient \( k_s \) for \( \frac{D_s}{\Delta z} \) into Equation (6.53) gives the maximum voltage which may be applied across the stack without exceeding the limiting current density.

\[
U_{\text{st}} \leq NA \left[ \frac{C_s^d}{C_s^c} + 1 + \frac{\Lambda_s C_s^d}{\Delta} \left( r^{\text{cm}} + r^{\text{am}} \right) \right] \frac{k_s F}{|z_i| \nu_i \left( T_i^m - T_i \right)} \Lambda_s
\]

(6.54)
Introducing Equation (6.54) into Equation (6.53) and (6.52) leads to a relation for the minimum membrane area required for a certain electrodialysis process.

\[
A = YX \geq \frac{\ln \left( \frac{C_s^f C_s^c}{C_s^f C_s^d} \right)}{\frac{1}{\Delta} \left[ \frac{C_s^d}{C_s^c} \left\{ \frac{C_s^f - C_s^d}{C_s^c} \right\} \right] + \frac{1 + \frac{\Lambda_s C_s^d}{\Delta} \left( r_{cm} + r_{am} \right)}{C_s^c \left( \frac{C_s^d}{C_s^c} + 1 + \frac{\Lambda_s C_s^d}{\Delta} \left( r_{cm} + r_{am} \right) \right) C_s^c + 1 + \frac{\Phi_s}{\Delta} C_s^c \left( T_{i1}^m - T_i \right) \frac{\nu_i}{\xi k_s}}}
\]

(6.55)

Here \( C \) is the salt concentration, \( \xi \) is the current utilization as given by Equation (), \( A \) is the area of the cell pair, \( Y \) is the cell width, \( X \) is the cell length and \( \Delta \) is the cell thickness as depicted in Figure , \( z \) the valence, \( \nu \) the stoichiometric coefficient, \( F \) the Faraday coefficient and \( Q \) is the total diluate volume passing through the stack. It is identical with the production capacity of the stack. The superscripts \( f, c \) and \( d \) refer the feed, concentrate and diluate; the subscripts \( s \) and \( i \) refer to salt and cat- or anions.

The required minimum length in a cell to achieve a certain product concentration is obtained by dividing Equation (6.55) by the cell width. Furthermore, the volume flow velocity \( Q \) can be expressed by the linear flow velocity \( u \) multiplied by cell width \( Y \) and the cell thickness \( \Delta \), i.e. \( u = \frac{Q}{Y \Delta} \).

The minimum cell length is then:

\[
X \geq \frac{\ln \left( \frac{C_s^f C_s^c}{C_s^f C_s^d} \right)}{\frac{1}{\Delta} \left[ \frac{C_s^d}{C_s^c} \left\{ \frac{C_s^f - C_s^d}{C_s^c} \right\} \right] + \frac{1 + \frac{\Lambda_s C_s^d}{\Delta} \left( r_{cm} + r_{am} \right)}{C_s^c \left( \frac{C_s^d}{C_s^c} + 1 + \frac{\Lambda_s C_s^d}{\Delta} \left( r_{cm} + r_{am} \right) \right) C_s^c + 1 + \frac{\Phi_s}{\Delta} C_s^c \left( T_{i1}^m - T_i \right) \frac{\nu_i}{\xi k_s}}}
\]

(6.56)

Equations (6.55) and (6.56) express the minimum required membrane area and cell length as a function of the plant capacity, feed and product concentration, membrane properties, the flow velocities of the diluate stream and a mass transfer coefficient determining the limiting current density.

The mass transfer coefficient can be related to the Sherwood number which is a function of the Reynolds number and thus a function of the linear flow velocity of the diluate stream. However, \( k_s \) is not a linear function of \( u \). Usually the mass transfer coefficient is express by:
Here $b$ is a constant which depends on the cell and spacer construction and has a value between 0.5 to 1. Thus the channel length is also a non linear function of the linear flow velocity of the dilute stream.

In an electrodialysis cell the mass transfer coefficient is difficult to determine from basic principles because of the influence of the spacer and cell geometry. For practical applications it is more convenient to express the limiting current density by a empirically derived relation:

$$i_{\text{lim}} = a \ u^b C_s^d$$  \hspace{1cm} (6.58)

Here $C_s^d$ is the diluate bulk solution concentration and $a$ and $b$ are constants. The constant $a$ includes membrane and solution properties, such as the transference numbers in the membrane and the solution, the salt diffusion coefficient in the solution, the temperature, etc. The constant $b$ is generally experimentally determined and a function of the spacer and cell geometry. In sheet flow cell construction $b$ has values between 0.4 and 0.7 and in tortuous path cell construction $b$ is between 0.6 and 0.9.

According to Equation (6.58) the limiting current density is a function of the diluate concentration. The diluate concentration, however, is changing during the desalting process while it passes from the feed solution entrance of the stack to the product exit. The limiting current density is decreasing accordingly along the flow path through the stack. The calculation of the minimum membrane area required for a given desalting capacity is based on an average limiting current density, which can be expressed by:

$$\hat{i}_{\text{lim}} = a \ u^b C_s^d = a \ u^b \frac{C_{s\text{fd}} - C_{s\text{p}}}{\ln \frac{C_{s\text{fd}}}{C_{s\text{p}}}}$$  \hspace{1cm} (6.59)

Here $\hat{i}_{\text{lim}}$ is an average limiting current density and $a$ and $b$ are constant factors, $u$ is the flow velocity of the diluate stream, $C_s^d$ is the average diluate concentration and $C_{s\text{fd}}$ and $C_{s\text{p}}$ are the diluate feed and product concentrations.

For constant cell geometry, membrane properties and applied voltage a rough estimation the required membrane area for a certain plant capacity can also obtained from a combination of Equations (6.52) and (6.59).
\[
A_{\text{total}} = \frac{z_i \nu_i F Q}{\xi^2} \left( C_s^f - C_s^d \right) = \frac{z_i \nu_i F Q \ln \left( \frac{C_s^f}{C_s^p} \right)}{\xi^2 a^u b}
\]

(6.60)

For a certain plant capacity, the required membrane area is directly related to the feed water concentration assuming the same product water concentration. This is illustrated in Figure 6.27, which shows a plot of the required membrane area to desalt 1 m\(^3\) of a feed solution per day, as a function of the feed solution concentration and product concentration.

Fig. 6.27 Required membrane area for a 1m\(^3\) per day plant capacity as function of the feed solution concentration assuming a product concentration of 0.4 g L\(^{-1}\) calculated by Equation (6.60). (The flow velocity is assumed to be 0.03 m s\(^{-1}\) and \(b = 0.5\))

For typical brackish water of ca. 3,000 ppm salt concentration and an average current density of 12 mA cm\(^{-2}\), the required membrane area for a plant capacity of 1 m\(^3\) product per day is ca. 0.4 m\(^2\) of cation- and 0.4 m\(^2\) of anion-exchange membranes. Other items such as pumps, piping, power supply and tanks do not depend on feed water salinity but on plant size. For desalination of brackish water with a salinity of ca. 3,000 ppm, the total capital costs for a plant with a capacity of 1,000 m\(^3\) per day can roughly be estimated to be in the range of US $200 to US $300 per m\(^3\) per day capacity taken the equipment prices of 1998. The cost of the actual membrane is less than 50 percent of the total capital investment. Assuming a useful life of five years for the membranes (up to seven years is common for many brackish water applications) and 10 years for the rest of the equipment, a feed water salinity of 3,000 ppm and a 24-hour
operating day, the total amortization of the investment is ca. US $ 0.10 to US $ 0.15 per m³ potable water with a salinity of less than 400 ppm.

The operating costs in electrodialysis are determined by the electrical energy required for the actual desalting process and the energy necessary for pumping the solution through the stack. The energy for the desalting process is a function of the amount of ionic species to be removed, as indicated in Equation (). The energy required to production of potable water with a concentration of less than 400 g/L as a function of the feed water concentration is shown in Figure .

![Diagram of energy requirements vs NaCl feed solution concentration](image)

**Fig. 6.29** Required energy for the desalination of 1 m³ feed solution as function of the feed solution concentration assuming a product concentration of 0.4 g L⁻¹ calculated by Equation () (The flow velocity is assumed to be 0.03 m s⁻¹ and b = 0.5)

The pumping energy is independent of the feed solution salinity, but it does depend on the feed water recovery rate and temperature. Assuming a pressure drop in the unit of ca. 400 kPa a pump efficiency of 70 % and 50 % recovery, the total pumping energy will be ca. 0.4 kWh per m³ product water. This indicates that at low feed water salt concentrations, the cost for pumping the solution through the unit might become quite significant.

It should be noted that the energy costs increase linearly with increasing current density while the required membrane area decreases in a hyperbolic function with the current density with increasing current density. Thus the total desalination cost - which is the sum of capital, energy and operating costs - will reach a minimum at a certain current density.

This is schematically shown in Figure 6.29. Here the energy costs, the amortization and the maintenance cost are shown as function of the applied current density.
The optimum operating current density in an electrodialysis process depends to a very large extend on the equipment and especially the membrane cost and membrane life in addition to the cost for basic energy. However, the current density to be applied in electrodialysis is only determined by economical considerations for technical reasons a certain maximum current density, i.e. the so-called limiting current density should not be exceeded as pointed out earlier. For low salt concentrations in the feed and the product the limiting current density is often significantly lower than the current density required for minimized total product costs.

6.2.6 Other electrical potential driven membrane processes

Although electrodialysis is today by far the most important industrial membrane separation process with an electrical potential gradient as driving force there are several other processes, such as regular electrolysis used for the production of chlorine and caustic soda, the electrodialysis with bipolar membranes used for the production of acids and bases from the corresponding salts, or the combination of conventional electrodialysis with regular ion-exchange techniques to produce ultra pure water. Most of these processes have been developed only recently and their large scale industrial utilization is still in the beginning with the exception...
of the chlorine/alkaline electrolysis which a state-of-the-art process and used since many years on a large industrial scale.

6.2.6.1 The chlorine-alkaline electrolysis

The electrolytic production of chlorine and caustic soda using a cation-exchange membrane as a separation media is gaining increasing technical and commercial significance. The principle of the process is illustrated in the schematic drawing of Figure 6.30, which shows an electrolysis cell arrangement consisting of two chambers separated by an cation-exchange membrane.

![Schematic diagram illustrating the chlorine/alkaline production process](image)

Fig. 6.30 Schematic diagram illustrating the chlorine/alkaline production process

One compartment contains an anode and a sodium chloride feed solution. The other compartment contains the cathode and at the beginning of the process water. When an electrical potential difference between the two electrodes is applied, the positively charged sodium ions will migrate towards the cathode producing hydrogen and hydroxyl ions in an electrochemical reaction at the cathode. The negatively charged chloride ions move towards the anode and will be oxidized to form chlorine. Thus, sodium chloride is electrochemically converted into chlorine, caustic soda, and hydrogen. A migration of the hydroxyl ions is prevented by the cation-
exchange membrane separating the anode from the cathode compartment. Thus, the current utilization in the electrolytic chlorine and caustic soda production is close to 100 %. The compartment containing the produced sodium hydroxide is usually operated in a feed and bleed mode and its sodium hydroxide concentration is kept as high as possible. In industrial production processes sodium hydroxide concentrations in excess 10 wt % are obtained. Since the sodium chloride concentration is also kept rather high the electrical resistance of the solutions is comparatively low, and the cell system can be operated at relatively high current densities up to a few thousand A/m². The main problem in the electrolytic production of chlorine and caustic soda is the stability of the cation-exchange membrane which faces a strong caustic environment on one side and solution containing free chlorine on the other side. Today, membranes based on fluorinated hydrocarbon polymers, such as the so-called Nafion®, have demonstrated useful life times of several years in operation, even at elevated temperatures.

6.2.6.2 Electrodialytic water dissociation in bipolar membranes
Bipolar membranes have recently gained increasing attention as efficient tools for the production of acids and bases from the corresponding salts by electrically forced water dissociation. The process, which has been known for many years, is economically very attractive and has a multitude of possible applications. So far, however, the large-scale use of the process has been rather limited because of the shortcomings of today’s bipolar membranes, which have to meet certain requirements as far as their water dissociation capability, their electrical properties, and chemical stability are concerned. But recent progress in the development of efficient bipolar membranes have increased the technical and industrial importance of this process.

a) Principle of water dissociation in bipolar membranes
The water dissociation in a bipolar membrane is illustrated in Figure 6.31 which shows a bipolar membrane consisting of an anion- and a cation-exchange layer arranged in parallel between two electrodes. If an electrical potential difference is established between the electrodes all charged components will be removed from an aqueous interphase between the two ion-exchange layers. If only water is left in the solution between the membranes further transport of electrical charges can only be accomplished by protons and hydroxyl ions which are available in very low concentrations of approximately 10⁻⁷ mol/L in completely deionized water.
Fig. 6.31: Schematic diagram illustrating the principle of electrically forced water dissociation in bipolar membranes

Protons and hydroxyl ions removed from the interphase between the cation- and anion-exchange membranes are replenished because of the water dissociation equilibrium.

b) Energy requirements and practical system design

The theoretical energy required for the process is that for establishing the desired concentration of H\(^+\) and OH\(^-\) ions in the outer phases of the membrane from their concentration in the membrane which is approximately 10\(^{-7}\) mol/L. The free energy of this process is:

\[
\Delta G = zRT \ln \frac{a_{H^+}a_{OH^-}^i}{a_{H^+}a_{OH^-}^o}
\]  

(6.61)

Here \(\Delta G\) is the free energy, \(z\) the valance, \(R\) the gas constant, \(T\) the absolute temperature, and \(a\) the activity. The superscripts \(o\) and \(i\) refer to the outside surface and the interphase between cation- and anion-exchange membrane, respectively.

For the generation of a one molar ideal solution of H\(^+\) and OH\(^-\) ions, i.e., \(a_{H^+}^o = 1\), \(a_{OH^-}^o = 1\), and \(z = 1\), Equation (6.61) reduces to:
\[ \Delta G = RT \ln \left( \frac{a_i^{\text{H}^+}}{a_i^{\text{OH}^-}} \right) = RT \ln K_w \]  

(6.62).

Here \( K_w \) is the dissociation constant of water.

For electrolyte solutions the free energy can be related to the electromotive force by:

\[ \Delta G = z F \Delta E \]  

(6.63)

Here \( F \) is the Faraday constant, \( z \) is the valence, and \( E \) is the reversible electromotive force.

Combining equations (6.62) and (6.63) leads to:

\[ \Delta E = \frac{RT}{F} \ln K_w \]  

(6.64)

The free energy and the electromotive force for the generation of \( \text{H}^+ \) and \( \text{OH}^- \) from water in a perfectly semi-permeable membrane can be calculated by equations (6.63) and (6.64), respectively.

At 25 °C the negative logarithm of the water dissociation constant, \(- \log K_w\) is 13.997. The free energy for the dissociation of one mole water and thus the production of one molar acid and base at 25 °C is:

\[ \Delta G = 79887 \text{ Joule} = 0.0222 \text{ kWh} \]

The reversible electromotive force for the process is:

\[ \Delta E = 0.828 \text{ Volt} \]

The actual potential drop across the bipolar membrane is always higher because of irreversible effects due to the electrical resistance of the bipolar membrane.

The generation of acid and base via an electrolysis process, however, requires considerably more energy. This is evident from the very nature of the process which entails co-production of \( \text{H}_2 \) and \( \text{O}_2 \) or chlorine as indicated in Figure 6.30 This step requires some additional energy input.

The theoretical energy in electrolysis varies slightly, depending on the particular salt being processed, the concentration of acid and base generated, and the temperature of operation. For production of one normal acids and bases at 25 °C the theoretical free energy varies between 0.056 and 0.58 kWh./mole The electromotive force thus varies between 2.1 and 2.2 Volts at 25 °C. For a practical electrolysis process, however, significantly larger amounts of energy must be provided to overcome the overvoltage for gas release at the electrodes.
To minimize the irreversible energy losses in a bipolar membrane its electrical resistance should be as low as possible. Further more in practical applications, bipolar membranes are exposed to an aggressive chemical environment. The cationic side of the bipolar membrane is facing a strong acid with pH-values of less than 1 and on the anionic side of the membrane is in contact with a strong base having pH-values in excess of 14. The preparation of cation-exchange membranes with excellent stability even in strong acid is relatively easy. Anion-exchange membranes with the required alkaline stability and electrical properties especially at elevated temperature are far more difficult to make and only recently bipolar membranes with long term stability at pH-values in excess of 13 have become available commercially. These membranes can be operated at current densities in excess of 1000 Am^{-2} with good current utilization.

A typical arrangement of an electrodialysis stack with bipolar membrane as used for the production of an acid and a base is illustrated in Figure 6.32 which shows the production of an acid HX and a base MOH from a salt MX. A repeating cell unit in this arrangement consist of three individual cell. 100 to 200 repeating cell units may be place between two electrodes in industrial size stacks.

![Electrodialysis cell arrangement with bipolar membranes for the production of an acid and a base from the corresponding salt](image)

Fig.6.32: Electrodialysis cell arrangement with bipolar membranes for the production of an acid and a base from the corresponding salt

6.2.6.3 Diffusion dialysis
Another process utilizing ion-exchange membranes in an electrodialysis stack cell arrangement is referred to as diffusion dialysis. In this process in principle identical to dialysis with the exception that ion exchange membranes are used and that therefore the ions in the solution the electroneutrality requirement must be fulfilled at all times. The primary driving force for the transport of ions is a concentration difference in two solutions separated by an ion-exchange membrane which leads to the build-up of an electrical potential so that certain ions may be transported even against their concentration gradient. The principle of the process is shown schematically in Figure 6.33.

![Diagram of diffusion dialysis](image)

**Fig. 6.33:** The principle of Diffusion- or Donnan-dialysis illustrating the transport Cu$^{++}$-ions through a cation-exchange membrane utilizing a diffusion potential build up by the flux of H$^{+}$-ions

Figure 6.33 shows a CuSO$_4$ solution and 1 n H$_2$SO$_4$ separated by a cation-exchange membrane. Since the H$^{+}$-ion concentration in the acid solution (') is significantly higher (pH = 1) than the H$^{+}$ ion concentration in coppersulfate solution (") (pH = 7) there will be a constant driving force for the flow of H$^{+}$-ions from solution (') into solution ("). Since the membrane is permeable to cations only there will be a build up of an electrical potential which will counterbalance the concentration difference driving force of the H$^{+}$-ions. This electrical potential difference which
is referred to as diffusion potential will cause a flux of Cu\textsuperscript{++-}ions against their concentration gradient from solution (\textquoteright\textquoteright) into solution (\textprime). As long as the H\textsuperscript{+}-ion concentration difference between the two phases separated by the cation-exchange membrane is kept constant, there will be a transport of Cu\textsuperscript{++-}ions until their concentration difference is of the same order of magnitude as the H\textsuperscript{+}-ion concentration difference. The fundamentals of diffusion dialysis have been discussed earlier. In praxis in it is applied in the same way as dialysis without ion-exchange membranes. A device is composed of an array of cells with the feed and the dialysate solution. It is usually operated in co- or counter-current flow.

The process can be carried out accordingly with anions through anion-exchange membranes. An example of anion diffusion dialysis is the sweetening of citrus juices. In this process hydroxyl ions furnished by a caustic solution replace the citrate ions in the juice.

6.2.7 Other membrane separation processes

There are a number of other membrane processes such membrane distillation, membrane pertraction and several hybrid processes combining different membrane process with each other or with conventional separation processes. But these processes shall not be discussed further in this outline.

References