

2 THEORY OF TRANSPORT IN MEMBRANES

2.1 Driving forces for transport mechanisms

A membrane process is a separation process that covers a broad range of problems from particles to molecules and a wide variety of membranes are available to design a process. Although the membranes may vary in material (organic vs. inorganic) and structure (porous vs. nonporous) the basic principle of membrane separation is the same. The separation process and mass transport through the membranes is a function of the membrane being used and the constituents being separated, and subsequently the theory used to describe the process and mechanisms. However, common for all systems is the principle illustrated in Figure 1 where a membrane is considered a permselective barrier, or interface between two phases, and the separation process takes place due to a specific driving force transporting a compound through the membrane from the one phase to the other.

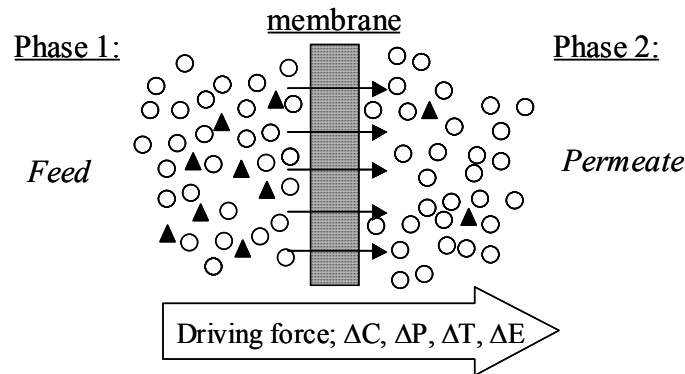


Figure 1. Schematic of membrane separation process with different driving forces that are present

The membrane separation process is defined by which compound is more readily transported (selectivity) through the membrane and by the flow of the specific compound (flux). Though this may occur by various mechanisms the performance and efficiency of the process is described by these parameters. The selectivity of a membrane is generally expressed as a retention factor (R) or by a separation factor (α). The definition of the retention factor is given by equation (0);

$$R = \frac{C_{feed} - C_{permeate}}{C_{feed}} = 1 - \frac{C_{permeate}}{C_{feed}} \quad (0)$$

where: C is the solute concentration in each phase noted.

Retention is often used for dilute aqueous solutions where the solvent is the water. As the retention is a dimensionless unit it expresses a percent that varies between 100% and 0%, where $R=100\%$ means a complete retention of the solute while $R=0\%$ means both the solute and the solvent pass equally through the membrane. The separation efficiency of gas mixtures and organic mixtures is generally expressed by the separation factor. For a binary mixture of

compounds A and B, the separation factor is expressed by the respective concentrations in the feed (x_A, x_B) and permeate (y_A, y_B) as expressed by equation (2);

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \quad (2)$$

The selectivity is chosen such that its value is greater than unity and it is expressed by which component passes through the membrane, *i.e.* for $\alpha_{A/B}$ the permeation rate of compound A is greater than compound B. If $\alpha_{A/B} = \alpha_{B/A} = 1$, no separation is achieved.

Given a membrane selectivity, the flow through a membrane, or flux, is defined by the driving force that governs the transport mechanism. When a membrane is the permselective barrier between two phases the transport of a molecule or particle across from one phase to the other will depend on a force that acts on the molecule or particle. The amount of force acting on the constituents will depend on the gradient in potential, or the difference in potential, across the membrane. The chemical potential difference ($\Delta\mu$) and the electrical potential difference are the main potential differences in membrane processes. [Mulder, 1997] The driving force is generally determined by the difference in chemical potential and is a result of either pressure differences across the membrane, concentration gradients between the two phases or from temperature differences. The electro potential difference is mainly important in electro dialysis and similar processes.

The definition of the chemical potential relates back to the thermodynamic principles that stem from Gibbs free energy equations. [Mulder, 1997; Baker *et.al.*, 1995; Sirkar/Ho (eds) *et.al.*, 1992] For isothermal conditions the chemical potential is determined by pressure and concentration, and the chemical potential is expressed as in equation (3)

$$\mu_i = \mu_i^o + RT \ln a_i + V_i P \quad (3)$$

Where μ_i^o is a constant expressing the chemical potential of the pure compound while a_i is the concentration of the compound in terms of activity, $a_i = \gamma_i x_i$ and determined by the activity coefficient and mole fraction. V_i is the volume of compound i and P the pressure, R is the universal gas constant and T temperature. The difference in chemical potential is therefore determined by a concentration term and pressure. This potential difference can be expressed as a differential as in equation (4);

$$\Delta\mu_i = RT\Delta \ln a_i + V_i\Delta P \quad \text{or} \quad d\mu_i = RTd \ln a_i + V_i dP \quad (4)$$

The chemical potential across a membrane is defined as the chemical potential on the permeate side minus the chemical potential on the feed side. From thermodynamics, diffusion (*i.e.* mass transport of a compound) is defined as spontaneous only if the change in chemical potential of the diffusing species is negative. A driving force from the feed side of a membrane to the permeate side can therefore be generated by decreasing the pressure on the permeate side or pressurizing the feed side.

Although thermodynamics is fundamental in understanding and describing a membrane process it is not sufficient for describing the transport phenomena. Various transport models have been developed based on the principles of thermodynamics and the structure and characteristics of the membrane. The simplest classification of membranes by structures is either as porous or as nonporous and the following presentation of models is based on this distinction. Some models, however, may be applied for both types of membranes.

2.2 Membrane transport models

2.2.1 Transport through porous membranes

An overview of various membrane manufacturing methods and membrane materials is presented in section **Error! Reference source not found.** From the combination of manufacturing method with the choice of membrane material it is apparent that the definition of a porous membrane is somewhat arbitrary. Pore sizes vary from 2 nm to greater than 10 μm and the shape and structure of the pore is quite different for the various membrane types. Although transport models have been developed for porous membranes one needs to be aware of the variety of existing pore geometries and membrane characteristics that influence the transport mechanisms. These characteristics have to a certain degree been incorporated into the respective models. With porous membranes, all transport from the feed to the permeate side is essentially through the pores rather than the dense matrix of the membrane. Subsequently, various membrane characteristics related to structure such as pore size, pore distribution, porosity, pore structure and the geometry of the pore need to be taken into consideration in developing a transport model.

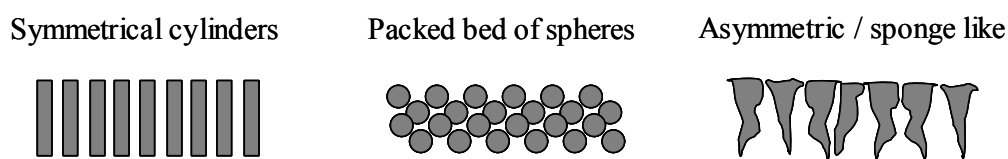


Figure 2. Schematic of basic pore geometries found in porous membranes

A schematic of basic pore geometries is shown in Figure 2. Two basic geometries are shown that possibly represent the two extremes, though in reality pore geometries are not as clearly defined and have many variations in between these structures. The simplest geometry is a series of regular cylindrical pores that are perpendicular to the membrane surface. In an idealized membrane of cylindrical pores with the same radius, the volume flux through the membrane may be described with the Hagen-Poiseuille equation.

$$J = \frac{\varepsilon \cdot r_p^2}{8 \cdot \mu \cdot \tau} \cdot \frac{\Delta P}{\Delta x} \quad (5)$$

where: ε is the surface porosity
 τ is the tortuosity
 μ is the viscosity
 r_p is the pore radius
 ΔP is the pressure difference across the membrane
 Δx is the membrane thickness (pore length)

For cylindrical pores the tortuosity is equal to unity. As the shape of the pore changes determining the tortuosity factor of a membrane is difficult. From equation (5) it is apparent that the morphology and characteristics of a membrane structure are important and influence the transport across the membrane. The equation gives a good description of well-defined parallel pores, however, such structures are not common in reality and the challenge is defining the parameters describing the membrane characteristics.

The opposite of this symmetrical shape is the porous structure that is formed when spherical shapes are packed in a bed to form a porous media. This structure is typically found in sintered and some phase inversion membranes. Several researchers have investigated flow through a porous media, particularly flow in sand-beds for filtration and groundwater flow. An expression for flow through a porous media of packed spheres has been developed by Carmen-Kozeny and is shown in equation (6);

$$J = \frac{\varepsilon^3}{K \cdot \mu \cdot S^2 \cdot (1-\varepsilon)^2} \cdot \frac{\Delta P}{\Delta x} \quad (6)$$

where; ε the volume fraction of the pores (bed porosity)
 K is the Carmen-Kozeny constant
 S the internal surface area
 μ is the fluid viscosity
 ΔP is the pressure difference across the membrane
 Δx is the membrane thickness (porous media thickness)

In most practical cases equation (6) is not easy to use either as the equation parameters are very much dependent on the geometry of the pores. This is a function of the media grain size, shape of the grains (sphericity), packing density etc. that define the membrane characteristics and subsequently it is difficult to evaluate these equation parameters.

Further investigation of the flow through pores show that the transport of molecules through porous membranes can be described by the mechanisms of convective flow, Knudsen diffusion and pore surface diffusion. When the pores are much larger than the molecule, transport will be by convective flow. However, if the pore size is smaller than the mean free path the convective flow is replaced by Knudsen diffusion. The mean free path (λ) is defined as the average distance traversed by a molecule between collisions. Knudsen diffusion is primarily a phenomenon that occurs in gas transport in porous media. In liquids molecules are

very close to each other and the free mean path is in order of a few Ångstroms. [Mulder, 1997] Knudsen diffusion can therefore be neglected in liquids for the finest porous membranes and will only be important for gases under certain conditions. These mechanisms are not included in the two transport models described above. As it primarily applies to gases, the principles of gas transport in porous membranes are illustrated in Figure 3. In convective flow (also called Poiseuille flow) all the gases flow through the membrane and no separation occurs. When the pores are very small and the mean free path of the gases is larger than the pore diameter, collisions with the pore wall occur. Under such circumstances the lighter molecules will then preferentially pass through the membrane. When the pore is sufficiently small, molecular sieving takes place excluding molecules that are larger than the pore size.

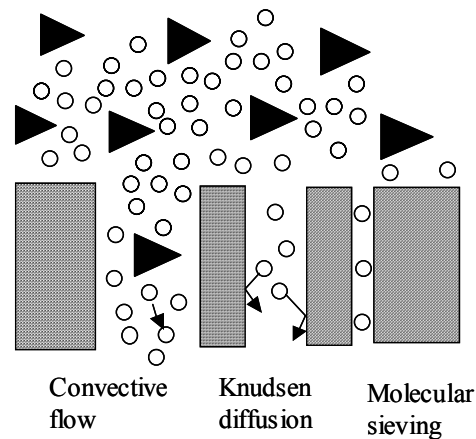


Figure 3. Mechanisms for gas flow through a microporous membrane as a function of pore size

When considering gas or vapor separation with porous membranes it is therefore important to determine which transport mechanism shown in Figure 3 is dominant or controlling the mass transport. The mean free path of gas molecules is a function of pressure and temperature and is given by;

$$\lambda = \frac{k \cdot T}{\pi \cdot d^2 \cdot P \cdot \sqrt{2}} \quad (7)$$

where; T is the temperature
 P is the pressure within the membrane pore
 d is the diameter of the gas molecule
 k is the Planck constant

Under atmospheric conditions and for pore diameters around 0.01 μm Knudsen flow was found to be dominant in gas flow through microporous membranes. [Callahan, 1988]

Considering the Hagen-Poiseuille and Carmen-Kozeny models presented above, the equation parameters immediately before the $\Delta P/\Delta x$ term can be viewed as expressions for the hydraulic permeability expressed in terms of the membrane characteristics. The transport models for porous membranes can thus be modified to account for specific membrane structures or mechanisms such as Knudsen flow. When Knudsen flow is dominant, a transport model defining the flux as in equation (8) may be used. [Mulder, 1997]

$$J = \frac{\pi \cdot n \cdot r_p^2 \cdot D_K}{R \cdot T \cdot \tau} \cdot \frac{\Delta P}{\Delta x} \quad (8)$$

where; r_p is the pore radius
 n is the number of moles
 D_K is the Knudsen diffusion coefficient
 R is the universal gas constant
 T is the temperature
 τ is the tortuosity
 ΔP is the pressure difference across the membrane
 Δx is the membrane thickness (pore length)

2.2.2 Transport through nonporous membranes

Nonporous membranes are primarily made from organic polymers and the presentation in this section will therefore only refer to synthetic organic membranes. Nonporous membranes are defined as such that the membrane has a homogenous structure without any defined pores. However, on a molecular level the polymer matrix and structure of the molecular chains does result in a morphology that can be defined as “molecular pores”. This distinction will be referred to when discussing transport through different types of nonporous membranes. In simple terms, transport through nonporous membranes can be described as a solution-diffusion mechanism. Nonporous membranes are sometimes referred to as solution-diffusion membranes because the transport occurs when molecules dissolve into the membrane and diffuse across it. In principle the mechanism is the same whether the separation process is for liquids or gases. However, the solubility of liquids and gases into the membrane polymer is quite different, with liquids in general showing a higher affinity for polymers than gases, and the actual transport of a liquid or gas through the membrane is therefore different.

The transport of a gas, vapor or liquid through a membrane can be described by the permeability of a membrane, which is a function of the solubility and diffusivity of the compound in the membrane material. Permeability can be expressed as;

$$\text{Permeability (P)} = \text{Solubility (S)} \times \text{Diffusivity (D)} \quad (9)$$

The solubility is a thermodynamic parameter and will depend on whether it is a gas or liquid that is dissolving into the membrane. In general, the solubility of gases in a polymer is low and can be described by Henry’s Law but does not apply to liquids. The diffusivity term on the other hand is a kinetic parameter that defines how fast a dissolved component is transported through the membrane. The diffusivity is dependent on the molecule being transported and the geometry of the polymer membrane. Different transport models have been developed for nonporous membranes and the solution-diffusion model and the free-volume diffusion model are probably the most widely accepted. [Baker *et.al.*, 1995]

2.2.3 Solution-diffusion model.

The underlying assumptions of mass transport in a solution diffusion processes are the following three steps: [Nijhuis, 1990; Wijmans *et.al.*, 1995]

1. Selective uptake (sorption) of one of the components on the feed side of the membrane,
2. Selective transport (diffusion) through the membrane,
3. Desorption (evaporation) on the permeate side of the membrane in the vapor phase.

In the solution-diffusion model the starting point to describe the kinetics of the diffusion process is based on thermodynamics where the driving force is related to the potential difference. The flux of a component can then be described by the following equation;

$$J = -L_i \frac{d\mu_i}{dx} \quad (10)$$

where; the differential is the chemical potential gradient of compound i
 L_i is a proportionality coefficient

In equation (10) the proportionality coefficient links the chemical potential to the flux. The chemical potential driving force in this expression can be any of the forces (concentrations, pressure, temperature, electrical), however, for most applications this can be restricted to concentration and pressure as expressed by equation (4). For incompressible phases (liquids) the volume doesn't change with pressure and integrating equation (4) gives;

$$\mu_i = \mu_i^o + RT \ln a_i + V_i (P - P_i^o) \quad (11)$$

For compressible phases (gas), the molar volume changes as a function of pressure. The ideal gas laws need to be applied when integrating equation (4) and gives;

$$\mu_i = \mu_i^o + RT \ln a_i + V_i \ln \frac{P}{P_i^o} \quad (12)$$

therefore described by Fick's first law.

$$J = -D \frac{dC}{dx} \quad (13)$$

where: J is the flux
 D is the diffusivity
 C is the concentration gradient over distance x .

Integrating this expression over the membrane thickness (l) we get the following expression, where C_f and C_p are the component concentrations at the membrane interface; [Boddeker, 1995]

$$J = \frac{D(C_f - C_p)}{l} \quad (14)$$

A variation of the solution-diffusion model is a modification that takes into account imperfections in a nonporous membrane. During manufacture fine pores may form through which mass transport may occur. The solution-diffusion-imperfection model includes a flow through these pores as well as the diffusion term. [Sherwood *et.al.*, 1967] The model has been used to describe the mass transport in reverse osmosis membranes, however, it has not been found suitable for design estimations of applications. [Soltanieh *et.al.*, 1981]

2.2.4 Free volume diffusion model.

This model was first proposed in the early 1960's and has since been developed by several studies. [Sirkar/Ho (eds) *et.al.*, 1992] Several investigators have attempted to develop a simple and useful version of the theory, however, providing a precise definition for the free-volume parameters has been difficult. The theory states that the movement of molecules within a matrix depends on the free volume available as well as the energy to overcome the polymer-polymer interactions. The definition of free volume is therefore dependent on whether a polymer is in the glassy or rubbery state. The state of a polymer is important in defining the free volume in this theory.

The state is defined as the phase in which the polymer appears. The phase of a polymer can be distinguished with two regions defined as rubbery or glassy polymers. For non-crystalline or amorphous polymers there is a transition temperature where the polymer changes from a glassy to a rubbery state. These states are determined by structural factors relating to polymer chain flexibility, chain interaction and molecular weight. A rubbery polymer is an amorphous polymeric material that is above its softening or glass transition temperature while a glassy polymer is below this temperature. [Billmeyer, 1971]

2.2.5 Resistance-in-series model

The transport models presented in sections 2.2.1 - 2.2.4 have been discussed based on the definition of porous and nonporous membranes. These transport models can be described as using a phenomenological approach or a mechanistic approach to describe a membrane separation process. The first group does not give any information on how the actual separation occurs while the second tries to relate the process to specific structure related parameters of the membrane. As discussed in previous sections, membranes are manufactured for specific applications and have a large variety in structure and composition such that a simple definition porous / nonporous is not always valid. In many cases, membranes will have characteristics and properties that can be related to both a porous and nonporous definition. Ultimately the need for a more general transport model is apparent which can be used for various applications.

A resistance-in-series model has been proposed that defines how the mass transfer of a component (liquid/liquid or liquid/gas) from one phase to another encounters a resistance. [Keller *et.al.*, 1967] With the development of composite membranes for gas separation processes a resistance model was also defined for these types of membranes. [Henis *et.al.*, 1981] By analogy to electrical circuits, transport across a membrane from one phase to the other needs to overcome a set of stages or resistances. The effective resistance to mass transport is then the sum of all the resistances. A key to the resistance-in-series model is therefore the identification of the various resistances to mass transport and the definition of each resistance.

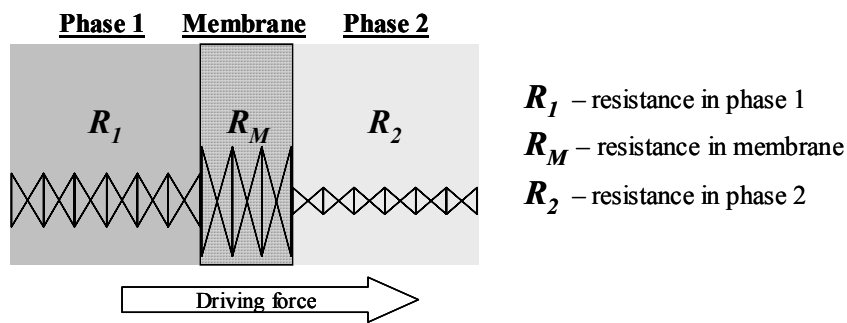


Figure 4. Schematic showing principle of resistance-in-series theory

The principle for a resistance in series model is illustrated in Figure 4 where the overall resistance to transport is the sum of a series of resistances in each phase. The resistance in phase 1, which is normally the feed, can be caused by the formation of a cake layer on the surface of the membrane or by liquid-film boundary layer effects such as concentration polarization or gel formation. The membrane resistance will inevitably be a function of the membrane structure (porous vs. nonporous) and various fouling phenomena. In phase 2, the resistance will relate to how efficient the permeating component is removed from the membrane. The overall resistance to mass transport in a membrane process will therefore be a function of the separation application (liquid vs. gas) and the specific properties of the membrane used in the process. For all cases, the reciprocal of the overall resistance will be equal to the sum of the reciprocal resistances defined for a system as expressed by equation (15);

$$\frac{1}{R_{overall}} = \frac{1}{R_1} + \frac{1}{R_M} + \frac{1}{R_2} \quad (15)$$

where: R_1 is the resistance in phase 1 (f.ex. liquid phase)
 R_M is the resistance in membrane (liquid or gas)
 R_2 is the resistance in the phase 2 (f.ex. gas phase)

The resistance-in-series model can be applied to both porous and nonporous membranes. The definition of the membrane resistance will depend on the membrane properties and needs to be defined for each application. For a nonporous membrane, the membrane resistance can be expressed by the permeability and the fiber thickness. In porous membranes, the pore size and geometry will determine if the transport is by convective flow, Knudsen diffusion or

molecular diffusion. In composite membranes, consisting of both a porous support layer and a dense membrane a combination of the above is required.

With the development of composite membranes and gas separation processes variations of the resistance in series model have been reported. The primary distinction between these applications of the model is related to the definition of the resistances and incorporating them in the overall resistance term. [Kimmerie, 1991; Ashworth, 1992; He *et.al.*, 1996] When the resistance to mass transfer is due to concentration polarization the resistance-in-series model is some times referred to as the stagnant film model. This is particularly the case for pressure-driven processes where the convective flow transports solute or particles to the membrane surface where they are retained and accumulate. [Zidney, 1992; Zidney, 1997] A similar approach is also applied between a liquid phase and gas phase when a porous membrane is used to create a phase interface, where the model is often referred to as the two-film model from the theory of gas transfer developed by Whitman and Lewis, 1924. An extension of the model is also been proposed where the model is modified to incorporate the additional resistance due to the membrane and characteristics of the transport phenomena. [Datta *et.al.*, 1992]

The resistance-in-series model is commonly used to define membrane contactors. [Sirkar/Ho (eds) *et.al.*, 1992; Noble/Stern (eds) *et.al.*, 1995; Gabelman *et.al.*, 1999] In vacuum degassing, the resistance-in-series model is therefore the most appropriate model to be applied as various membrane types can be accounted for and the resistances to mass transfer can be defined for each phase as a function of the system. In the following section, a resistance-in-series model will be used to describe the three basic membrane separation designs, hydrophobic/hydrophilic microporous membranes and composite/dense nonporous membranes.

2.3 Transport model applied to gas transfer

The resistance-in-series model has been chosen to describe the mass transport in a degassing application using a membrane contactor. When a vacuum is applied to one side of a gas permeable membrane that is immersed in water, a concentration gradient is created across the membrane. Dissolved gases in the water diffuse in the direction of decreasing concentration, through the membrane and into the vacuum. With hydrophilic microporous membranes the pores are wetted by the water and are filled by the solute. In the case of hydrophobic microporous membranes the pores are generally gas-filled and provide the interface between the vacuum and liquid phase. For hydrophobic membranes the pores will remain dry and gas-filled as long as the penetration pressure is not exceeded. The critical pressure at which wetting of the pores occurs is referred to as the breakthrough pressure. [Kiani *et.al.*, 1984; Kim *et.al.*, 1987; Nirmalakhandan *et.al.*, 1987; Gabelman *et.al.*, 1999] The breakthrough pressure for a liquid/liquid phase or gas/liquid phase has been reported as in equation (16).

$$\Delta P = \frac{2\gamma \cos \theta}{r_p} \quad (\text{liquid/liquid}), \quad \Delta P = \frac{2\sigma \cos \theta}{r_p} \quad (\text{gas/liquid}) \quad (16)$$

Here γ is the interfacial tension and σ the surface tension, while θ is the contact angle and r_p is the pore radius. Relating to a gas/liquid phase, this pressure is therefore a function of the surface tension, the contact angle and the pore diameter. The contact angle is defined as the

angle measured in the wetting fluid that forms between the wetting fluid and membrane pore. [Osipow, 1962] The relative breakthrough pressure for various membrane configurations and gas/liquid interactions have been reported in Noble/Stern (eds) *et.al.*, 1995. The significance of the breakthrough pressure is apparent in a vacuum degassing system. In vacuum degassing it is important that the aqueous phase is not pulled through the membrane pores and into the gas phase as this is contradictory to the objective. The pores will remain dry and gas-filled in a water/vacuum application in hydrophobic membranes if the pores are very small, $< 0.1 \mu\text{m}$. In this study, hydrophobic membranes were therefore used and analysis of the resistance-in-series model that applies is therefore based on situation A in Figure 5.

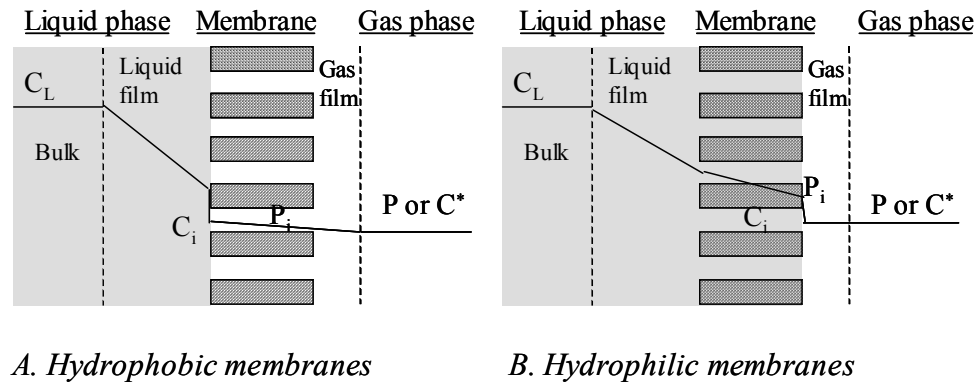


Figure 5. Partial pressure and concentration profiles for a gas/liquid phase with: *A.* gas-filled pores, and *B.* liquid-filled pores

A membrane contactor as shown in Figure 5 is essentially used as a phase barrier between the gas and liquid phases, where a hydrophobic membrane prevents the liquid phase from entering the pores. Under a vacuum the pores remain dry and gas filled while under pressure the barrier may prevent bubbles from entering the liquid. As long as the liquid pressure is equal to or higher than the gas pressure bubbles will not form. In effect, the membrane serves to create a phase interface between the gas/liquid interface and an equilibrium separation process of either gas absorption or gas stripping will take place depending on the direction of the driving force.

The kinetics of gas transfer modeled using the resistance-in-series model, is therefore like the two-film theory for mass transport across and gas/liquid interface with the addition of a membrane resistance. [Letterman (ed), 1999] The mass transfer of gases across a membrane is therefore determined by three resistances in series as shown in Figure 6. These consist of a resistance across the liquid-film layer created by the aqueous solution around the fibers, the resistance of the membrane, and finally the gas-film layer created by the gases within the fiber. The sum of these resistances defines the overall resistance to gas transfer with a microporous membrane system. The reciprocal of the overall resistance is the overall mass transfer coefficient of the system.

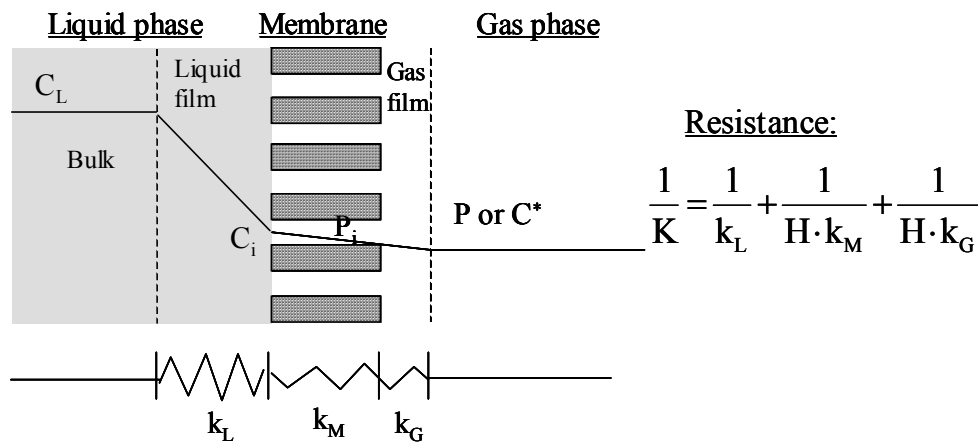


Figure 6. Mass transfer resistance in the respective phases of a microporous hydrophobic membrane.

Analysis of a hydrophobic porous membrane is illustrated in Figure 6 where the dissolved gases being removed encounter a resistance in the liquid boundary layer, the gas-filled pores of the membrane and the gas phase boundary layer. A gas-liquid interface is formed between the aqueous phase and gas phase at the pore openings. The concentration profile of any gas across the membrane and is discontinuous at the liquid-gas interface, and can be expressed by the equilibrium condition defined by Henry's law. The equilibrium relationship over the interface is expressed by equation (17);

$$C_{i_{water}} = H \cdot C_{i_{gas}} \quad (17)$$

where: C is the interface concentration in the water and gas phase
 H is partition coefficient expressed by Henry's law constant

In vacuum degassing, the driving force for mass transfer is from the liquid phase to the gas phase. The over all mass transfer coefficient and individual mass transfer coefficients for a hydrophobic membrane, based on the aqueous phase concentration are then expressed as; [Sirkar/Ho (eds) *et.al.*, 1992]

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{H \cdot k_M} + \frac{1}{H \cdot k_G} \quad (18)$$

where: K is the overall mass transfer coefficient
 k_L is the liquid-film mass transfer coefficient
 k_M is the membrane mass transfer coefficient
 k_G is the gas-film mass transfer coefficient
 H is Henry's law constant

The terms on the right hand side of equation (18) represent the resistance to mass transfer in the two boundary layers and the membrane. Development of this equation also assumes the following; a steady state system, equilibrium exists at the interface, the pores are uniform through out the membrane, no transport occurs through the nonporous parts of the membrane, and mass transfer can be described by simple film-type mass transfer coefficients.

The mass transport across the membrane can be described by the flux. The flux can be defined for each layer taking into account the individual mass transfer coefficients. In principle, the flux through each defined layer must be the same and the respective fluxes are equal. In this way the interface concentrations can be eliminated and the flux may be expressed in terms of the overall mass transfer coefficient and the concentration gradient between the bulk concentrations in the liquid phase and the gas phase. For a steady state condition the flux of gases across the membrane during vacuum degassing may be calculated using the formula:

$$N = K(C - C^*) \quad (19)$$

where: K is the over all mass transfer coefficient
 C is the liquid phase bulk concentration
 C^* is the gas phase concentration

The over all mass transfer efficient, K , is determined by the type of membrane used, and the appropriate expression representing the respective mass transfer resistances that dominate the overall resistance to mass transfer. From an evaluation of equation (18) one can see that resistance to mass transfer may be controlled by one or several stages, depending on the value of the respective mass transfer coefficients and the partition coefficient. For example, if the mass transfer coefficients in each phase (liquid-membrane-gas) are in the same order of magnitude, the value of the partition coefficient will be important. In gas transfer, the value of Henry's law constant will determine the significance of the membrane resistance and gas-film boundary layer. For soluble or sparingly soluble gases the value of Henry's law constant is high, and thus the second and third term in equation (18) become negligible, and the resistance in the liquid-film boundary becomes dominant.

The mass transfer characteristics and individual mass transfer coefficients for microporous gas-permeable hollow-fibers have been studied and the results indicate that the mass transfer coefficient is always controlled by the resistance in the liquid phase [Yang *et.al.*, 1986]. This is due to the nature of the hydrophobic microporous membranes. Gas-phase diffusion is several orders of magnitude greater than liquid-phase diffusion, 10^4 times faster than liquid phase diffusion [Cussler, 1997]. The resistance in the gas-phase boundary layer can therefore be neglected. Gas transfer through hydrophobic membranes is by gas-phase diffusion and the membrane resistance can be negligible. As with aeration systems, the overall mass transfer can thus be estimated by evaluating the liquid-film transfer coefficient, k_L . Several investigators have developed mass transfer correlations for aeration using hollow fiber membranes [Sirkar/Ho (eds) *et.al.*, 1992; Noble/Stern (eds) *et.al.*, 1995; Perry, 1997]. Since degassing is simply the reverse process of aeration, the same correlations can be applied to the vacuum degassing system. The overall mass transfer coefficient may therefore be determined by calculating the Sherwood number (Sh) based on these correlations.

2.4 Analyzing and predicting mass transfer coefficients

2.4.1 Experimental analysis of mass transfer coefficients

An alternative method to determine the membrane resistance for a system as well as getting some insight to the effect of the fluid velocity on the individual mass transfer coefficients is the Wilson plot method. [Wislon, 1915; Prasad *et.al.*, 1988] The assumption is that the mass transfer coefficient is proportional to the fluid velocity, v^α , where the exponential α is an empirical constant for a given system. The Wilson plot gives a straight line when the mass transfer coefficient is plotted against the fluid velocity as K^{-1} vs. $v^{-\alpha}$. For hydrophobic membranes the resistance from the gas phase boundary layer can be neglected and the Wilson plot is made with data collected at high fluid velocities. The intercept represents the membrane resistance from which the membrane mass transfer coefficient can be determined. The Wilson plot is illustrated in Figure 7. The data used in the plot is from this study to determine the membrane resistance for the composite membranes tested; reference chapter **Error! Reference source not found.**, section **Error! Reference source not found.** for details.

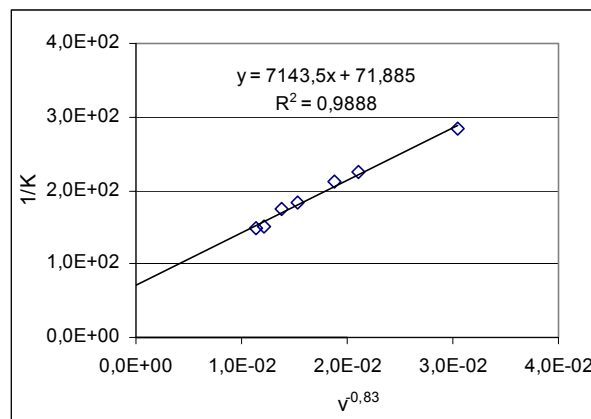


Figure 7. Example of a Wilson plot to determine the membrane mass transfer resistance, k_M .

2.4.2 Predicting mass transfer coefficients

Describing the mass transfer coefficients of any degassing system or membrane contactor process is important for the design of a unit. Correlations describing the mass transfer coefficients of different types of mass transfer equipment have been developed, including various membrane module configurations. In general, the mass transfer coefficient is described using equation (20) and can be used to predict the performance of a system. [Noble/Stern (eds) *et.al.*, 1995; Perry, 1997]

$$Sh \propto a \cdot Re^\alpha \cdot b \cdot Sc^\beta \quad (20)$$

where: Sh is the Sherwood number
 Re is the Reynolds number
 Sc is the Schmidt number
 a, b, α, β are functions of geometry

The functions in equation (20) are system dependent for membrane processes and the respective values are specific for a module configuration and mode of operation, i.e. feed flow outside or inside tubular modules, co-current/counter-current/cross-flow modes etc. By definition the dimensionless numbers (Sh , Re and Sc) are expressed in equations (21) – (23).

$$Sh = \frac{k_L d_e}{D} \quad (21)$$

$$Re = \frac{v_L d_e}{\nu} \quad (22)$$

$$Sc = \frac{\nu}{D} \quad (23)$$

where: k_L is the liquid-film mass transfer coefficient
 d_e is the hydraulic diameter or effective diameter
 D is the liquid diffusion coefficient of the component
 v_L is the liquid velocity past the membrane
 ν is the kinematic viscosity of the liquid

By convention the hydraulic diameter for hollow fiber membranes is expressed as,

$$d_e = \frac{4 \times \text{cross sectional area}}{\text{wetted perimeter}} \quad (24)$$

Several investigators have reported correlations based on equation (20) to predict the mass transfer coefficient for a given unit design. For the sake of comparison of correlations the membrane processes have been grouped as follows; tube side flow, shell side flow parallel to the fibers and shell side cross-flow. The summary is shown in Table 1.

The Schmidt number (Sc) is in fact a correction factor for temperature such that the different mass transfer coefficients may be compared at a normalized temperature. [Geankoplis, 1972] As can be seen from the summary of selected correlations reported in the literature, listed in Table 1, the correction factor is Sc raised to the 0.33 power.

Correlation	Comments	Reference
Tube side flow:		
$Sh=1.62(d^2v/LD)^{1/2}$	General L�ev�eque solution	L�ev�eque, 1928
Shell side parallel flow:		
$Sh=\beta[d_e(1-\phi)/L]Re^{0.6}Sc^{0.33}$	For $0 < Re < 500$, $0.04 < \phi < 0.4$ and $\beta=5.8$ or 6.1	Prasad <i>et.al.</i> 1988
$Sh=1.25(Re d_e/L)^{0.93}Sc^{0.33}$	For $0 < Re < 500$, $\phi=0.26$, 0.03	Yang <i>et.al.</i> 1986
$Sh=8(Re d_e/L)Sc^{0.33}$	Channeling suspected, questionable accuracy	Dahuron <i>et.al.</i> 1988
$Sh=0.019Gz$	For $Gz < 60$ for close packed fibers	Wickramasinghe, 1992
$Sh=(0.53-0.56\phi)Re^{0.53}Sc^{0.33}$	For $21 < Re < 324$, $0.32 < \phi < 0.76$	Costello <i>et.al.</i> 1993
$Sh=0.18Re^{0.81}Sc^{0.33}$	For $600 < Re < 46000$, $\phi=0.01$, 0.03	Letterman. 1999
Shell side cross-flow:		
$Sh=0.15Re^{0.8}Sc^{0.33}$	For $Re > 2.5$ (cylindrical, helical wound)	Wickramasinghe, 1992
$Sh=0.12Re^{0.8}Sc^{0.33}$	For $Re < 2.5$ (cylindrical, helical wound)	Wickramasinghe, 1992
$Sh=6.0Gz^{0.35}$	For $Gz > 11$ crimped flat membrane	Wickramasinghe, 1992
$Sh=1.25Gz$	For $Gz < 11$ crimped flat membrane	Wickramasinghe, 1992
$Sh=1.38Re^{0.34}Sc^{0.33}$	For $1 < Re < 25$, $\phi=0.70$	Prasad <i>et.al.</i> 1988
$Sh=0.90Re^{0.40}Sc^{0.33}$	For $1 < Re < 25$, $\phi=0.07$	Prasad <i>et.al.</i> 1988
$Sh=0.61Re^{0.363}Sc^{0.333}$	For $0.6 < Re < 49$, $\phi=0.003$	C�ot�e <i>et.al.</i> 1989
$Sh=1.45Re^{0.32}Sc^{0.33}$	Developed for bubbleless aeration	Ahmed <i>et.al.</i> 1996
$Sh=0.24(Re d_e/L)^{0.59}Sc^{0.33}$	Developed for sealed fibers in jet stream	Johnson <i>et.al.</i> 1997
$Sh=0.39Re^{0.29}[WeEu]^{0.39}Sc^{0.33}$	Developed for bubbleless surface aeration	Weiss <i>et.al.</i> 1996
$Sh=0.9Re^{0.5}Sc^{0.33}$	For $1 < Re < 1000$ (rectangular module)	Crespo <i>et.al.</i> 1994

Note: ϕ is the packing fraction. WeEu = gauge feed pressure x pore diameter/water surface tension.

Table 1. Summary of correlations developed for different membrane module configurations and modes of operation.

Tube side flow:

Investigations of mass transfer in membrane contactors with tube side flow have shown that the L ev eque-solution can be used to predict the performance reasonably well. [Gabelman *et.al.*, 1999]

Shell side flow parallel to the fibers:

Mass transfer in a hollow fiber membrane contactor is analogous to heat transfer in a shell-and-tube exchanger. A general term referring to heat transfer has been developed which can be applied to mass transfer as expressed in equation (25) [Knudsen *et.al.*, 1958];

$$Sh = 0.022 \cdot Re^{0.6} \cdot Sc^{0.33} \quad (25)$$

Although this term represents a fairly good description of the mass transfer it was not found suitable to predict experimental data. [Wickramasinghe *et.al.*, 1992] The discrepancy was attributed to effects of module geometry that are not included in equation (25). Variations of the equation have been developed by several investigators to include geometrical factors and operating conditions that take into account the module configuration, packing densities, flow regimes and so forth. [Yang *et.al.*, 1986; Dahuron *et.al.*, 1988; Prasad *et.al.*, 1988; Wickramasinghe *et.al.*, 1992; Costello *et.al.*, 1993; Letterman (ed), 1999] One of the problems related to shell side flow parallel to the fibers is channeling effects around the fibers and fluid flow profiles along the fibers. The definition of the fluid velocity is important as the mass transfer coefficient is a function of the local fluid velocity along the fibers.

Shell side flow with cross-flow:

With the first membrane contactors that were developed the controlling resistance to mass transfer was primarily controlled by the resistance in the membrane. With the development of new materials and improved membrane manufacturing techniques the permeability of the membrane has improved drastically and attention has been given to reduce other resistances to mass transfer. Particularly the shell side boundary layer has been investigated resulting in alternative modes of operation using cross-flow. [Gabelman *et.al.*, 1999]