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INVITED REVIEW PAPER

Fundamentals of membrane transport

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Abstract−A review is presented to give a generalized membrane transport theory based on the principles of nonequilibrium thermodynamics. This theory is then used to develop specific flux equations for gas separation, pervaporation, osmosis, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, dialysis, and electrodialysis. All membrane processes suffer from boundary layer mass transfer resistances caused by concentration polarization. The convective motions parallel and perpendicular to the membrane surface are distinguishable, and the former becomes more relevant than the latter in the boundary layer mass transfer. The modified Péclet number is introduced and its importance is discussed in characterizing the boundary layer mass transfers of various membrane processes. Many different transport mechanisms through membrane itself are reviewed including the solution-diffusion model, pore model, permeation through composite membranes, and transport through inorganic membranes. Finally, the differences between membrane mass transfer and other mass transfer are delineated, including a discussion of negative mass transfer coefficient.

Key words: Membrane Transport, Nonequilibrium Thermodynamics, Concentration Polarization, Modified Péclet Number

INTRODUCTION

Membrane separation, though relatively new, is a widely used unit operation in many industries, including water treatment for both drinking and waste water, pharmaceuticals, textiles, pulp and paper, biotechnology, food and beverages, chemical industry, metallurgy, automotive; health care delivery, and environmental applications. A variety of different membrane operations are employed in practice: gas separation (GS), pervaporation (PV), osmosis (OS), reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), dialysis (D), electrodialysis (ED), membrane distillation (MD), and membrane contactors (MC). Membrane processes are particularly advantageous for the separation and purification of biological molecules since the operating environment requires no harsh conditions such as high temperatures or pressures, and it does not involve phase changes or chemical additives. Thus membrane processes cause minimal denaturation, deactivation, and/or degradation of highly labile biological cells or macromolecules.

In all cases of membrane separations, selective mass transfer makes the desired separation possible under one or more of driving forces such as pressure, concentration, temperature, and electrical potential differences. The two important aspects that affect the economy of a given membrane process are selectivity and flux. Since the ideal selectivity is determined by the ratio of fluxes involved, the flux equation is the most crucial entity in any membrane process. There are many flux equations representing specific membrane permeation processes in the literature, but not many unified theories exist.

Therefore, the aim of this review is to present a generalized membrane transport theory and give a specific flux equation for each membrane process, and to accentuate the difference between mass transfer and other transport phenomena through examples of membrane transport.

OVERALL TRANSPORT IN MEMBRANE PROCESSES

1. Resistance in Series Model

When mass transfer takes place through a membrane system, the penetrant molecule must go through not only the membrane itself but also all of the other layers surrounding the membrane, such as the boundary layers, which present additional resistances to the mass transfer process. If the penetrant is a liquid, the boundary layer resistances are especially significant and cannot be ignored. Based on the analogy between the mass transfer process and electrical circuit, the overall mass transfer resistance can be calculated as the sum of individual resistances through each layer, except in some cases that are discussed at the end of this review:

$$\frac{1}{K}=\frac{1}{k_{l1}}+\frac{1}{k_m}+\frac{1}{k_{l2}} \tag{1}$$

where K is the overall mass transfer coefficient, k_{l1} and k_{l2} are the mass transfer coefficients through each boundary layer in the upstream and downstream sides, and k_m is the mass transfer coefficient of membrane itself. If the membrane consists of several layers, such as in the case of a laminate composite membrane that includes most of the polymeric and inorganic membranes, the total membrane resistance must be calculated as the sum of individual resistances:

$$\frac{1}{k_m}=\frac{1}{k_{m1}}+\frac{1}{k_{m2}}+\frac{1}{k_{m3}}+\cdots \tag{2}$$

where k_m is the overall membrane mass transfer coefficient, and k_{m1}, k_{m2}, etc., are the mass transfer coefficients through each composite layer. For example, the two-layer model frequently represents the most high flux membranes, which consist of a thin dense top layer and a thick porous support layer. Thus, the overall mass transfer

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coefficient should be calculated based on the mass transfer coefficients of two boundary layers, the dense top layer and porous support layer, using the above two equations.

To make the above arguments valid, an implicit assumption is made: the driving force of the mass transfer operation should be a general one, such as chemical potential difference, and it is also a continuous function that corresponds to the voltage in an electrical circuit.

2. Driving Forces

There are many different driving forces available for various membrane processes. Traditionally, for each membrane process a specific flux equation describing that particular membrane transport was employed with a particular driving force. A unified approach regarding the driving forces and flux equations is seldom utilized, and consequently this situation confuses beginning scientists. For a given membrane process, one must choose an appropriate driving force in order to determine the correct flux equation that describes correctly the membrane transport in question.

For gas separations achieved with membranes, the partial pressure difference is the driving force; in dialysis the driving force is the concentration difference; the fugacity difference is the driving force for pervaporation; and in reverse osmosis both the hydraulic pressure difference and osmotic pressure difference are driving forces. The voltage difference must be considered along with the concentration difference as the driving forces for electrodialysis. These seemingly complicated situations can be unified if the chemical potential difference is used as the universal driving force [1].

For any membrane process one may start with a chemical potential difference as the driving force. This can be converted to other specific driving forces that are appropriate to the specific membrane process under consideration. These conversions are necessary since the final flux equation must contain only proper, measurable quantities. The abstract quantities such as chemical potential, fugacity, and activity are not as useful as pressure, concentration, osmotic pressure, etc., which are all measurable in the laboratory. The interrelationships among these different driving forces are defined by the equilibrium thermodynamic definitions. As shown in Fig. 1, the chemical potential difference under an isothermal process may be expressed either in terms of the fugacity difference or the activity difference:

$$\Delta\mu_i = \mathrm{RT}\Delta(\ln \mathrm{f}_i) = \bar{\mathrm{V}}_i\Delta\mathrm{P} + \mathrm{RT}\Delta(\ln \mathrm{a}_i) \tag{3}$$

Here μ_i, f_i, $\bar{\mathrm{V}}_i$, and a_i are the chemical potential, fugacity, partial molar volume, and activity of the species i in the solution respectively, and P and T are the pressure and temperature.

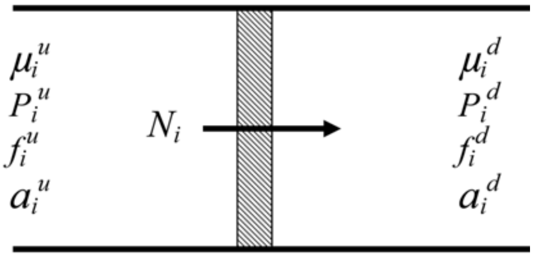

Fig. 1. Steady state membrane transport.

The fugacity difference is a useful driving force for gas permeation and pervaporation processes, as is the activity difference for all liquid membrane processes. The second line in the above equation is the integral form of the following differential expression of the chemical potential change for an isothermal process:

$$\mathrm{d}\mu_i = \left(\frac{\partial\mu_i}{\partial \mathrm{P}}\right)_{T,a_i}\mathrm{dP} + \left(\frac{\partial\mu_i}{\partial \mathrm{a}_i}\right)_{T,P}\mathrm{da}_i = \frac{\partial}{\partial \mathrm{n}_i}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{P}}\right)_{T,a_i}\mathrm{dP} + \left(\frac{\partial(\mathrm{RT}\ln \mathrm{a}_i)}{\partial \mathrm{a}_i}\right)_{T,P}\mathrm{da}_i = \bar{\mathrm{V}}_i\mathrm{dP} + \mathrm{RTd}(\ln \mathrm{a}_i) \tag{4}$$

Here G is the total Gibbs' free energy.

In special cases the driving forces may become nonlinear quantities: for hydrogen permeation through a palladium membrane or proton-conducting ceramic membranes the permeation flux is proportional to the square root of pressure difference [2-5] rather than the usual pressure difference. For oxygen permeation through certain ceramic membranes, the oxygen flux is similarly proportional to one-fourth of the power of pressure the difference [6-11]. These nonlinear pressure differences arise from the transport mechanisms that are specific to those membrane processes.

3. Nonequilibrium Thermodynamics

All membrane processes are nonequilibrium processes; therefore, the transport equation describing a particular membrane process must satisfy the principles of nonequilibrium thermodynamics. Consider a multicomponent membrane permeation process taking place across a membrane as shown in Fig. 1.

A one-dimensional problem can be treated without loss of the essential aspect of thermodynamic expressions; this can then be generalized for a three-dimensional case if necessary. At steady state, the molar flux N_i of species i with respect to the laboratory fixed coordinates is the number of moles of species i that passes through a unit area per unit time, which may be split into two terms [12]:

$$\mathrm{N}_i = \mathrm{c}_i\mathrm{v}_i = \mathrm{c}_i(\mathrm{v}_i - \mathrm{v}) + \mathrm{c}_i\mathrm{v} = \mathrm{J}_i^* + \frac{\mathrm{c}_i}{\mathrm{c}}\mathrm{N} = \mathrm{J}_i^* + \mathrm{x}_i(\text{or } \mathrm{y}_i)\mathrm{N} \tag{5}$$

Note that this expression should be treated as a point function (differential expression) since the values of J_i^* and x_i (or y_i) may vary as a function of position while N_i and N stay constant at steady state. Summing up for all i, we obtain $\sum_i \mathrm{J}_i^* = 0$.

If the rate of entropy production per unit area is σ due to the membrane process, the rate of lost work is $\mathrm{T}\sigma$, which must be the same as the rate of Gibbs' free energy loss due to membrane transport under a steady state and constant temperature process [1]:

$$\mathrm{T}\sigma = -\frac{\mathrm{d}\Delta \mathrm{G}}{\mathrm{dt}} = -\left[\sum_i \mathrm{N}_i\mu_i^d - \sum_i \mathrm{N}_i\mu_i^u\right] = -\sum_i \mathrm{N}_i\Delta\mu_i \tag{6}$$

Using Eqs. (3) and (6) for gas permeation, this can be expressed as:

$$\mathrm{T}\sigma = -\sum_i \mathrm{N}_i\mathrm{RT}\Delta(\ln \mathrm{f}_i) \tag{7}$$

Similarly for liquid membrane processes,

$$\mathrm{T}\sigma = -\sum_i \mathrm{N}_i\bar{\mathrm{V}}_i\Delta\mathrm{P} - \sum_i \mathrm{N}_i\mathrm{RT}\Delta(\ln \mathrm{a}_i) = -\mathrm{q}\Delta\mathrm{P} - \sum_i \mathrm{N}_i\mathrm{RT}\Delta(\ln \mathrm{a}_i) \tag{8}$$

where the total volumetric flux q, which may be constant for a steady state process for an incompressible fluid, is introduced.

$$\mathrm{q} = \sum_i \mathrm{N}_i\bar{\mathrm{V}}_i \tag{9}$$

There are three principles of nonequilibrium thermodynamics [13-16]. For the first principle, the rate of lost work should be a scalar product of all fluxes and forces:

$$T\sigma=\sum_i J_iX_i \tag{10}$$

According to the second principle, the fluxes are a linear combination of all forces:

$$J_i=\sum_i L_{ij}X_j \tag{11}$$

The final principle postulates the Onsager reciprocal relationship:

$$L_{ij}=L_{ji} \tag{12}$$

The above three equations will play a central role in membrane transport phenomena.

4. Ideal Gas Permeation

Gas permeation is caused by a pressure difference across the membrane. This irreversible process will create an entropy production, according to Eq. (7). When Eq. (7) is used, all variables are interpreted as those of bulk fluids.

When the fugacity is replaced by the partial pressure, $\bar{P}_i$ in Eq. (7), the rate of lost work for ideal gas permeation can be rewritten as:

$$T\sigma=-\sum_i N_i\Delta\mu_i=-\sum_i N_iRT\Delta(\ln f_i)\approx-\sum_i N_iRT\Delta\ln\bar{P}_i \tag{13}$$

Any of the above expressions may be used as a starting point in developing the nonequilibrium thermodynamics of ideal gas permeation. When Eq. (5) is substituted into the above equation, care must be exercised because the former is a differential form and the latter is an integral equation. The correct way of doing this is to take a differential form of Eq. (13) and combine the two equations, making it an integral form as shown below:

$$Td\sigma=-\sum_i N_iRTd\ln\bar{P}_i=-\sum_i(J_i^*+y_iN)RTd\ln(y_iP) \tag{14}$$

Recognizing the following identities,

$$\sum_i J_i^*=0 \tag{15}$$

$$\sum_i y_id\ln y_i=\sum_i dy_i=0 \tag{16}$$

Eq. (14) can be rewritten as:

$$Td\sigma=-\sum_i J_i^*RTd(\ln y_i)-NRTd(\ln P) \tag{17}$$

Thus the integral form becomes:

$$T\sigma=-\sum_i J_i^*RT\Delta(\ln y_i)-NRT\Delta(\ln P) \tag{18}$$

As shown in the above developments, there can be many different forms of $T\sigma$, which results in a variety of choices of fluxes and forces that describe the gas permeation systems. The following example illustrates this situation.

4-1. Example 1. Binary Gas Permeation

The first choice of fluxes and forces may be made for ideal gas permeation from Eq. (13), which can be rewritten for a binary system as:

$$T\sigma=-N_1RT\Delta(\ln\bar{P}_1)-N_2RT\Delta(\ln\bar{P}_2)$$

$$=-N_1RT\ln\left(\frac{\bar{P}_1^d}{\bar{P}_1^u}\right)-N_2RT\ln\left(\frac{\bar{P}_2^d}{\bar{P}_2^u}\right) \tag{19}$$

Here superscripts d and u designate the downstream and upstream side of the membrane, respectively. The identification of fluxes and forces gives:

$$J_1=N_1 \text{ and } J_2=N_2 \tag{20}$$

$$X_1=-\frac{RT\Delta\bar{P}_1}{\mathrm{lmdel}(\bar{P}_1)} \tag{21}$$

$$X_2=-\frac{RT\Delta\bar{P}_2}{\mathrm{lmdel}(\bar{P}_2)} \tag{22}$$

where the logarithmic mean values of partial pressures are introduced and defined by:

$$\mathrm{lmdel}(\bar{P}_1)\equiv\frac{\Delta\bar{P}_1}{\ln\left(\frac{\bar{P}_1^d}{\bar{P}_1^u}\right)} \tag{23}$$

$$\mathrm{lmdel}(\bar{P}_2)\equiv\frac{\Delta\bar{P}_2}{\ln\left(\frac{\bar{P}_2^d}{\bar{P}_2^u}\right)} \tag{24}$$

The linear relationship between fluxes and forces becomes:

$$N_1=-L_{11}\frac{RT\Delta\bar{P}_1}{\mathrm{lmdel}(\bar{P}_1)}-L_{12}\frac{RT\Delta\bar{P}_2}{\mathrm{lmdel}(\bar{P}_2)} \tag{25}$$

$$N_2=-L_{21}\frac{RT\Delta\bar{P}_1}{\mathrm{lmdel}(\bar{P}_1)}-L_{22}\frac{RT\Delta\bar{P}_2}{\mathrm{lmdel}(\bar{P}_2)} \tag{26}$$

When no cross phenomena exist, the above equations yield ordinary gas permeation equations:

$$N_1=-Q_1\Delta\bar{P}_1 \tag{27}$$

$$N_2=-Q_2\Delta\bar{P}_2 \tag{28}$$

with the following identifications of gas permeability coefficients:

$$Q_1\equiv L_{11}\frac{RT}{\mathrm{lmdel}(\bar{P}_1)} \tag{29}$$

$$Q_2\equiv L_{22}\frac{RT}{\mathrm{lmdel}(\bar{P}_2)} \tag{30}$$

The second choice of fluxes and forces is made from Eq. (18). Due to the nature of the binary system, $J_1^*+J_2^*=0$ the first term in Eq. (18) becomes:

$$\sum_i J_i^*RT\Delta(\ln y_i) = J_1^*RT\Delta\ln(y_1/y_2) \tag{31}$$

Substituting Eq. (31) into Eq. (18) yields:

$$T\sigma=-NRT\Delta(\ln P)-J_1^*RT\Delta\ln(y_1/y_2)$$

$$=-NRT\left(\ln\frac{P^d}{P^u}\right)-J_1^*RT\left(\ln\frac{y_1^dy_2^u}{y_1^uy_2^d}\right) \tag{32}$$

The physical significance of the above equation is rather interesting. The first term in the second line represents the rate of lost work due to pressure expansion of an ideal gas, and is always positive. The argument of the logarithm of the second term is the separation factor. Since according to convention the separation factor is greater than 1 and all other quantities in the second term are positive, the net value of the second term will always be negative. This means that the separation will reduce the entropy production rate, or in other words, the irreversibility. Thus diffusion causes separation: the greater the amount of separation, the less the resulting entropy production rate for the overall permeation process.

Thus the two independent fluxes are linearly related to their corresponding forces by:

$$N=L_{00}[-RT\Delta(\ln P)]+L_{01}[-RT\Delta\ln(y_1/y_2) \quad (33)$$

$$J_1^*=L_{10}[-RT\Delta(\ln P)]+L_{11}[-RT\Delta\ln(y_1/y_2) \quad (34)$$

Notice that in addition to the principal terms (the first term in Eq. (33) and the second term in Eq. (34)), which represent the conjugated phenomena, the cross terms (the other two terms) are also present in the total flux as well as in the diffusion flux expressions. These cross terms represent the coupling phenomena that are predicted by the nonequilibrium thermodynamic theory. For many membrane processes these coupling terms may be smaller than the principal (conjugated) terms, but in other cases they may be large enough to be included. Specifically, the first term in Eq. (34) indicates that pressure diffusion may be present when diffusion takes place under a large pressure drop. Clearly, Eqs. (33) and (34) show that the coupling phenomenon plays an important part in a gas permeation/diffusion system.

When the off-diagonal terms are not present or are negligibly small, the above equations yield the following expressions for total and diffusion fluxes:

$$N=-L_{00}RT\Delta(\ln P) \quad (35)$$

$$J_1^*=-L_{11}RT\Delta\ln(y_1/y_2) \quad (36)$$

The diffusion flux for the second species is not needed since its magnitude is identical to that of the first species, but negative. As in the previous case, Eq. (35) can be easily identified with the conventional expression for total flux under a pressure drop with the permeability coefficient (or filtration coefficient) as:

$$Q_0\equiv L_{00}\frac{RT}{\mathrm{lmdel}(\overline{P})} \quad (37)$$

The expression for diffusion flux requires a bit of transformation before it can be identified with the conventional formula. With the use of $y_1+y_2=1$, Eq. (36) can be rewritten as:

$$J_1^*=-L_{11}RT\left[\frac{1}{\mathrm{lmdel}(y_1)}+\frac{1}{\mathrm{lmdel}(y_2)}\right]\Delta y_1=-D_1\Delta c_1 \quad (38)$$

where

$$D_1\equiv\frac{L_{11}RT}{\overline{c}}\left[\frac{1}{\mathrm{lmdel}(y_1)}+\frac{1}{\mathrm{lmdel}(y_2)}\right] \quad (39)$$

It should be noted that Eq. (33) is for the total molar flux of binary gas mixture under a pressure drop. The driving force for diffusion in Eq. (36) is the separation factor, which is a new way of expressing the diffusion term in a gas separation. Conversely, if there is no diffusion with gas permeation, there will be no separation-a fact that has never been discussed in the literature.

The permeation flux equation given by Eq. (5) is a differential form. All variables in this equation are point functions at specific position in the membrane. When the average values of the upstream and downstream values are substituted in place of point functions, this equation becomes an integral equation. With the substitution of the diffusion and total flux expressions into Eq. (5) and using the average concentrations, the permeation flux for species i can be calculated by:

$$N_i=J_i^*+\frac{\overline{c}_i}{\overline{c}}N=-D_i\Delta c_i-\frac{\overline{c}_iQ_0}{\overline{c}}\Delta P \quad (40)$$

The above equation is very convenient when a distinction needs to be made between different types of driving forces for gas permeation. For example, binary counter permeation can take place in the absence of a pressure drop across a semi-permeable membrane. In this case the second term will drop out, leaving only the diffusion term. On the other hand, if a membrane with large pores is placed in between two different pressures, only the second term will be tion and no diffusion takes place; therefore no concentration difference is sustained.

The non-uniqueness of the entropy production rate expression means that there is freedom in the selection of the appropriate fluxes and forces. These flux equations show that coupling phenomena are possible in general for multi-component gas transport through a membrane. However, not many couplings have been reported in the literature, except for pressure diffusion; even pressure diffusion has not been treated as a coupling phenomenon.

5. Liquid Permeation (RO, NF, UF, MF, Dialysis, etc.)

The rate of lost work due to entropy production for any liquid phase permeation is given by Eq. (8):

$$T\sigma=-\sum_i N_iRT\Delta(\ln f_i)=-q\Delta P-\sum_i N_iRT\Delta(\ln a_i) \quad (41)$$

All quantities represented are for the bulk phases on either side of the membrane. Since the entropy production deals with the outcome of any process, it should involve only the state variables of a system before and after the process, such as $\Delta(\ln f_i)$, ΔP and $\Delta(\ln a_i)$. The advantage of this expression is that the nonequilibrium theory does not have to involve the activity within the membrane, the actual mechanisms of permeation.

5-1. Example 2. Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF), and Microfiltration (MF) for a Single Solute and Single Solvent

For the sake of simplicity, this discussion is limited to a binary system, where subscripts s and w represent solute and solvent, respectively. Using the van't Hoff equation for osmotic pressure (π),

$$\pi=RTc_s \quad (42)$$

a part of the driving force in the second term in the last expression of Eq. (41) for low solute concentration becomes:

$$RT\Delta(\ln a_s)\approx\frac{RT\Delta(\gamma_s x_s)}{\gamma_s\overline{x}_s}\approx\frac{RT\Delta x_s}{\overline{x}_s}\approx\frac{RT\Delta c_s}{\overline{c}_s}=\frac{\Delta\pi}{\overline{c}_s} \quad (43)$$

The activity coefficient is assumed to change very little between upstream and downstream.

When the above equation is combined with the Gibbs-Duhem equation:

$$\mathrm{RT}\Delta(\ln a_w) = -\frac{\bar{x}_s \mathrm{RT}\Delta(\ln a_s)}{\bar{x}_w} \approx -\frac{\mathrm{RT}\Delta x_s}{\bar{x}_w} \approx -\frac{\mathrm{RT}\Delta c_s}{\bar{c}_w} = -\frac{\Delta\pi}{\bar{c}_w} \tag{44}$$

With the substitution of Eqs. (43) and (44) into Eq. (41), the entropy production term now becomes:

$$\mathrm{T}\sigma = -q\Delta\mathrm{P} - \sum_i \mathrm{N}_i \mathrm{RT}\Delta(\ln a_i) = -q\Delta\mathrm{P} - \frac{\mathrm{N}_s\Delta\pi}{\bar{c}_s} + \frac{\mathrm{N}_w\Delta\pi}{\bar{c}_w} \tag{45}$$

A new flux can be defined as:

$$\mathrm{J}_D \equiv \frac{\mathrm{N}_s}{\bar{c}_s} - \frac{\mathrm{N}_w}{\bar{c}_w} \tag{46}$$

It should be noted that the above equation does not imply that the total flux is the same as the diffusion flux. The flux defined by Eq. (46) is widely used in RO, NF, UF, and MF, as shown originally by Katchalsky and Curran [17].

The entropy production term becomes:

$$\mathrm{T}\sigma = -q\Delta\mathrm{P} - \mathrm{J}_D\Delta\pi \tag{47}$$

The linear flux equations are:

$$-q = \mathrm{L}_P\Delta\mathrm{P} + \mathrm{L}_{PD}\Delta\pi \tag{48}$$

$$-\mathrm{J}_D = \mathrm{L}_{DP}\Delta\mathrm{P} + \mathrm{L}_D\Delta\pi \tag{49}$$

These are the standard equations used in the field after Katchalsky and Curran [17].

The reflection coefficient, r, is introduced, which is the measure of coupling between solvent and solute flows:

$$r \equiv -\frac{\mathrm{L}_{PD}}{\mathrm{L}_P} \tag{50}$$

The expression for total volume flux becomes the well-known form:

$$-q = \mathrm{L}_P(\Delta\mathrm{P} - r\Delta\pi) \tag{51}$$

This volume flux is used in conjunction with the following solute flux equation, which can be derived by combining Eqs. (46) through (51) and the definition of the "solute permeability" defined by Katchalsky and Curran [17]:

$$\omega \equiv -\left(\frac{\mathrm{L}_P\mathrm{L}_D - \mathrm{L}_{PD}^2}{\mathrm{L}_P}\right)\bar{c}_s \tag{52}$$

$$\mathrm{N}_s = \omega\Delta\pi + (1-r)q\bar{c}_s \tag{53}$$

In the fields of reverse osmosis, nanofiltration, and ultrafiltration, the total volume flux from Eq. (51) and the solute flux from Eq. (53) are widely used. The system is characterized by three parameters-filtration coefficient, L_P; reflection coefficient, r; and solute permeability, ω-as shown by Katchalsky and Curran [17] and later demonstrated by Narebska and Kujawski [18]. When negligible osmotic pressure is present, as in some cases of ultrafiltration and microfiltration, only the total volume flux, Eq. (51), is needed with the filtration coefficient.

Using the above example, we can clearly illustrate how the nonuniqueness of splitting fluxes and forces and the importance of coupling phenomena are manifested in nonequilibrium thermodynamics. The entropy production term for RO, NF, UF, and MF expressed by Eqs. (6) and (47) can be further changed to reflect the latest transformations of fluxes and forces:

$$\mathrm{T}\sigma = -q(\Delta\mathrm{P} - r\Delta\pi) - (rq + \mathrm{J}_D)\Delta\pi \tag{54}$$

The first term shows that the total volume flux q is driven by the difference of hydrodynamic and osmotic pressure difference, which is the net available driving force across a membrane. In the second term the newly defined flux, $(rq+\mathrm{J}_D)$, is too cumbersome to be used in the laboratory, but it can be converted to yield the solute flux given by Eq. (53). Both of these are the result of the coupling phenomenon from Eqs. (48) and (49). The off-diagonal terms play a central role in RO, NF, UF, and MF processes. Also, it is evident that the invariant entropy production term for the same process can have three different expressions as shown in Eqs. (6), (47), and (54); therefore, the split of fluxes and forces is not unique. When the coupling terms are not included, the system degenerates to a trivial ordinary filtration and diffusion, and the essence of RO is completely missing.

5-2. Example 3. Binary System of Dialysis

The convenient starting place for a binary dialysis system is Eq. (41). Ordinarily, no pressure drop is applied for dialysis, so Eq. (41) can be written as:

$$\mathrm{T}\sigma = \mathrm{N}_1\mathrm{RT}\Delta(\ln a_1) - \mathrm{N}_2\mathrm{RT}\Delta(\ln a_2) \tag{55}$$

The fluxes and forces are identified with negligible convective contribution as shown:

$$\mathrm{J}_1 = \mathrm{N}_1 \tag{56}$$

$$\mathrm{J}_2 = \mathrm{N}_2 \tag{57}$$

$$\mathrm{X}_1 = -\mathrm{RT}\Delta\ln a_1 \tag{58}$$

$$\mathrm{X}_2 = -\mathrm{RT}\Delta\ln a_2 \tag{59}$$

The linear relationship between fluxes and forces is:

$$\mathrm{N}_1 = -\mathrm{L}_{11}\mathrm{RT}\Delta\ln a_1 - \mathrm{L}_{12}\mathrm{RT}\Delta\ln a_2 \tag{60}$$

$$\mathrm{N}_2 = -\mathrm{L}_{21}\mathrm{RT}\Delta\ln a_1 - \mathrm{L}_{22}\mathrm{RT}\Delta\ln a_2 \tag{61}$$

When the off-diagonal terms are neglected and the activities are converted into concentrations with constant activity coefficients, the dialysis fluxes can be expressed as:

$$\mathrm{N}_1 = -\mathrm{D}_{D1}\Delta c_1 \tag{62}$$

$$\mathrm{N}_2 = -\mathrm{D}_{D2}\Delta c_2 \tag{63}$$

where D_{D1} and D_{D2} are the dialysis coefficients for species 1 and 2 and defined as:

$$\mathrm{D}_{D1} \equiv \frac{\mathrm{L}_{11}\mathrm{RT}}{\bar{c}_1} \tag{64}$$

$$\mathrm{D}_{D2} \equiv \frac{\mathrm{L}_{22}\mathrm{RT}}{\bar{c}_2} \tag{65}$$

6. Pervaporation

Pervaporation is a membrane separation process where the upstream side of the membrane is exposed to a liquid mixture while the downstream side is in contact with a vapor phase of low pressure. When the difference of the chemical potential is calculated, care must be exercised to account for the change of phases. The fugacity of species i on the liquid side is the product of the standard state fugacity and activity. The fugacity of species i on the vapor side at low pressure is the product of total pressure and mole fraction of species i in the vapor phase. Eq. (7) can be expressed for the pervaporation process as:

$$T\sigma=-\sum_i N_i RT\Delta(\ln f_i)=-\sum_i N_i RT\ln(f_i^d/f_i^u)$$

$$\approx-\sum_i N_i RT\ln\left(\frac{Py_i}{P_i^s\gamma_i x_i}\right) \tag{66}$$

Here, an ideal gas law was assumed for the vapor phase.

6-1. Example 4. Binary Pervaporation

The rate of lost work due to pervaporation is given by the previous equation:

$$T\sigma=-\sum_i N_i RT\Delta(\ln f_i)\approx-\sum_i N_i RT\ln\left(\frac{Py_i}{P_i^s\gamma_i x_i}\right)=\sum_i J_i X_i \tag{67}$$

In a binary pervaporation system, there is one solute and one solvent, which are represented by s and w, respectively. The identification of fluxes and forces gives:

$$J_1=N_s \text{ and } J_2=N_w \tag{68}$$

$$X_1\equiv-\frac{RT\Delta f_s}{\mathrm{lmdel}(f_s)} \tag{69}$$

$$X_2\equiv-\frac{RT\Delta f_w}{\mathrm{lmdel}(f_w)} \tag{70}$$

The fugacity differences between upstream and downstream sides for solute and solvent are:

$$-\Delta f_s=f_s^u-f_s^d=P_s^s\gamma_s x_s-Py_s \tag{71}$$

$$-\Delta f_w=f_w^u-f_w^d=P_w^s\gamma_w x_w-Py_w \tag{72}$$

The logarithmic mean delta values are defined as before:

$$\mathrm{lmdel}(f_s)\equiv\frac{\Delta f_s}{\ln\frac{f_s^d}{f_s^u}} \tag{73}$$

$$\mathrm{lmdel}(f_w)\equiv\frac{\Delta f_w}{\ln\frac{f_w^d}{f_w^u}} \tag{74}$$

The linear relationship between fluxes and forces are:

$$N_s=-L_{11}\frac{RT\Delta f_s}{\mathrm{lmdel}(f_s)}-L_{12}\frac{RT\Delta f_w}{\mathrm{lmdel}(f_w)} \tag{75}$$

$$N_w=-L_{21}\frac{RT\Delta f_s}{\mathrm{lmdel}(f_s)}-L_{22}\frac{RT\Delta f_w}{\mathrm{lmdel}(f_w)} \tag{76}$$

When the off-diagonal terms are neglected, the familiar expressions are produced for pervaporation:

$$N_s=Q_s(P_s^s\gamma_s x_s-Py_s) \tag{77}$$

$$N_w=Q_w(P_w^s\gamma_w x_w-Py_w) \tag{78}$$

where two permeabilities for solute and solvent are defined by:

$$Q_s\equiv-L_{11}\frac{RT}{\mathrm{lmdel}(f_s)} \tag{79}$$

$$Q_w\equiv-L_{22}\frac{RT}{\mathrm{lmdel}(f_w)} \tag{80}$$

In the pervaporation field, Eqs. (77) and (78) are widely used to describe the fluxes of solutes and solvents, respectively. The role of coupling phenomenon is emphasized in the application of nonequilibrium thermodynamics to pervaporation of alcohol and water by Kedem [19].

7. Electrodialysis

Electrodialysis is a membrane separation process in which an external electrical driving force is imposed (electrical potential difference) to drive ionic or charged species across a membrane. The rate of lost work in the absence of pressure drop is given by:

$$T\sigma=-\sum_i N_i\Delta\mu_i-I\Delta\phi=-\sum_i N_i RT\Delta\ln a_i-I\Delta\phi \tag{81}$$

Here I is electric current and $\Delta\phi$ is electric potential difference. If all fluxes were independent the flux equations would be written as:

$$I=L_{00}(-\Delta\phi)+\sum_j L_{0j}(-RT\Delta\ln a_j) \tag{82}$$

$$N_i=L_{i0}(-\Delta\phi)+\sum_j L_{ij}(-RT\Delta\ln a_j) \tag{83}$$

However, the electric current in this case is carried by the ionic species, and thus it can be expressed as:

$$I=\sum_i N_i\zeta_i F \tag{84}$$

Therefore, the lost work rate becomes:

$$T\sigma=-\sum_i N_i(RT\Delta\ln a_i+\zeta_i F\Delta\phi) \tag{85}$$

Compared to the above approach, it is much more convenient to introduce the total driving force as an electrochemical potential difference that combines the electromotive potential difference with the chemical potential difference term. The electrochemical potential $\tilde{\mu}_i$ for a species i with a charge of ζ_i under an external electric potential ϕ is defined as:

$$\tilde{\mu}_i\equiv\mu_i+\zeta_i F\phi \tag{86}$$

where F is the charge per mole of electrons, F=96,484.56. The lost work due to electrodialysis can be expressed from Eq. (41) with this modification:

$$T\sigma=-\sum_i N_i\Delta\tilde{\mu}_i=-\sum_i N_i(\Delta\mu_i+\zeta_i F\Delta\phi) \tag{87}$$

The first term in the last part of the above equation is identical to the case of ordinary dialysis and the second term is additional, due to the electrical interaction.

The linear flux equations can thus be written as below, ignoring all off-diagonal terms and the convective term:

$$N_i=-L_{ii}(RT\Delta\ln a_i+\zeta_i F\Delta\phi) \tag{88}$$

Or this equation can be approximated in terms of the concentration differences rather than the activity differences as:

$$N_i=-D_{Di}\left(\Delta c_i+\frac{\zeta_i F}{RT}\Delta\phi\right) \tag{89}$$

where L_{ii} is a phenomenological coefficient and D_{Di} is the dialysis coefficient for species i; these are interrelated by the following definition:

$$D_{Di} \equiv \frac{L_{ii}RT}{\bar{c}_i} \tag{90}$$

The hydraulic pressure difference plays little role in electrodialysis. Eq. (89) is conventionally used to describe the permeation flux in electrodialysis [3b].

There are many other membrane transport phenomena that are outside of the scope of this review, such as transport through cell membranes and charged membranes and topics of electro-kinetic effects across mixed-lipid membranes.

BOUNDARY LAYER TRANSPORT

1. Concentration Polarization

The permeating species of any membrane process must penetrate the stagnant boundary layer before going through the membrane. Every membrane separation process suffers from concentration polarization. In the stagnant boundary layer next to membrane, the concentration of the more permeable species is depleted as shown in Fig. 2. Thus the available driving force across the membrane is reduced, causing a flux decline.

On the other hand, the less permeable species accumulates on the surface of the membrane as illustrated in Fig. 3. This creates a concentration buildup, which in turn produces undesirable membrane fouling in many liquid phase operations. The selectivity also decreases, adding inefficiency to the separation process. All of these phenomena, which are due to the concentration polarization, increase the cost of membrane processes.

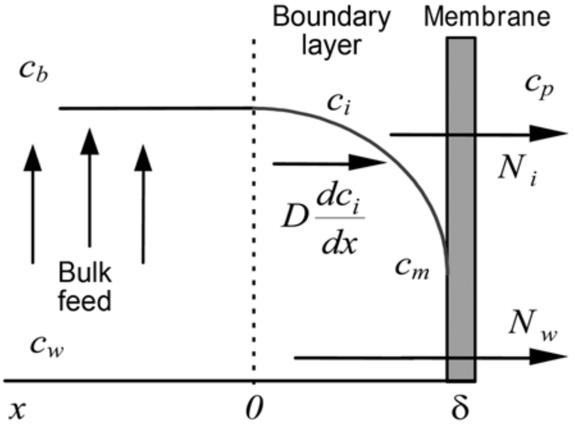

Fig. 2. Concentration profile of preferentially permeating component under steady state conditions.

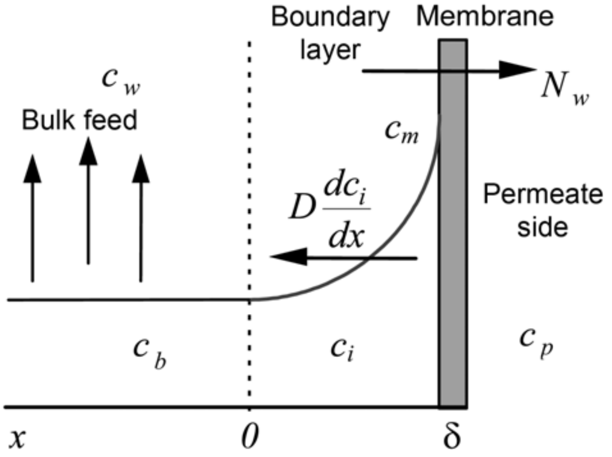

Fig. 3. Concentration profile of retained component under steady state conditions.

In both cases of Figs. 2 and 3, the concentration of the permeating species at the membrane surface, c_m, can be determined by integrating the differential flux equation within the boundary layer. In the boundary layer mass transfer takes place by two different mechanisms: one by diffusion and the other by bulk motion. When Fick's law is used and N/c is replaced with the total volumetric flux, q, Eq. (5) can be rewritten as:

$$N_i = J_i^* + \frac{c_i}{c}N = -D\frac{dc_i}{dx} + qc_i \tag{91}$$

This is Nernst-Planck equation. The first term represents diffusion flux and the second term shows how much convection (in the direction of flow) contributes to the total mass flux. Integration of this equation over the boundary layer thickness, assuming constant volumetric flux, diffusivity, and molar flux, $N_i = q\,c_p$, results:

$$\ln\left(\frac{c_m - c_p}{c_b - c_p}\right) = \frac{q\delta}{D} \tag{92}$$

Here the concentration polarization index is defined as:

$$I \equiv \frac{c_m}{c_b} \tag{93}$$

This is a measure of the degree of polarization. The separation factor for a dilute system can be approximated as:

$$\alpha \equiv \frac{y/(1-y)}{x/(1-x)} = \frac{N_i/(N-N_i)}{c_b/(c-c_b)} \cong \frac{qc_p}{c_bN/c} = \frac{c_p}{c_b} \tag{94}$$

Then Eq. (92) can be rewritten as:

$$\ln\left(\frac{I-\alpha}{1-\alpha}\right) = \frac{q\delta}{D} \tag{95}$$

As demonstrated in the equation above, the concentration polarization index is a function of the separation factor and convective and diffusive velocities. There are two extreme cases that are of interest.

The first case is for a very large separation factor, $1 \ll \alpha$. After the application of a Taylor expansion and truncation of the higher order terms, Eq. (95) may be approximated as:

$$\frac{q\delta}{D} = \ln\left(\frac{I/\alpha - 1}{1/\alpha - 1}\right) \cong \frac{1}{\alpha} - \frac{I}{\alpha} \tag{96}$$

Then the concentration polarization index becomes:

$$I \approx 1 - \frac{\alpha q\delta}{D} \approx 1 - \frac{\alpha q}{k} \tag{97}$$

Here the diffusivity over the boundary layer thickness is replaced by the mass transfer coefficient since the diffusion is the predominant mass transfer mechanism in this case. Later in this review Eq. (108) will corroborate this statement.

$$\frac{D}{\delta} \approx k \tag{98}$$

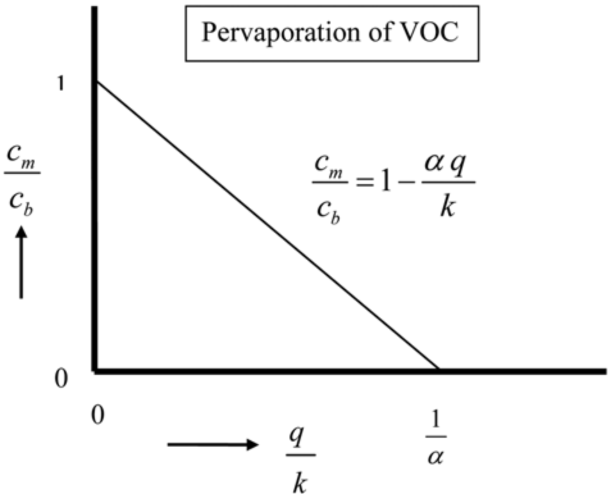

Fig. 4. Concentration polarization vs. q/k for pervaporation of volatile organic compound.

An example of this scenario is the volatile organic compound (VOC) separation from a dilute aqueous solution by pervaporation, where the separation factor is very large. The graphical representation of concentration polarization vs. q/k for VOC separation by pervaporation is shown in Fig. 4.

The second case is a very small separation factor system such as RO, NF, UF, and MF. Eq. (95) can be approximated by ignoring the α term as:

$$I \cong \exp\left(\frac{q\delta}{D}\right) \tag{99}$$

The graphical representation of concentration polarization as a function of qδ/D for RO, NF, UF, and MF is shown in Fig. 5.

As shown above, the concentration buildup for the retained component for these membrane processes can be significant. It should be noted that the overall mass transfer for the retained component is still directed in exact opposition to the concentration gradient within the boundary layer due to the high convective volumetric flux.

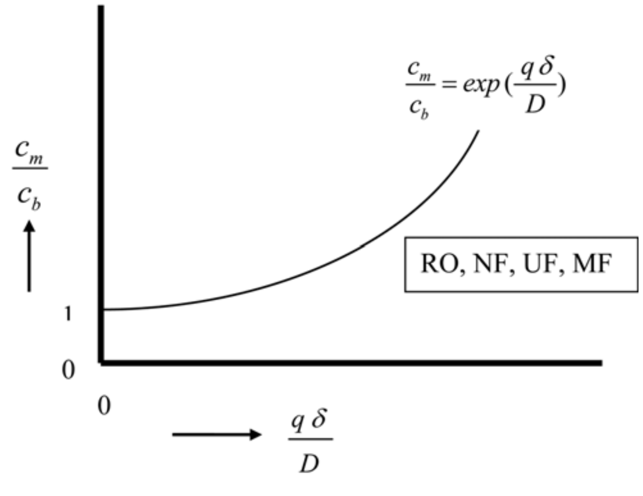

Fig. 5. Concentration polarization vs. qδ/D for reverse osmosis, nanofiltration, ultrafiltration, and microfiltration.

2. Mass Transfer Coefficient from the Sherwood Number

Based upon the hydrodynamic conditions outside of the boundary layer, an empirical method can be used to estimate the boundary layer mass transfer coefficient if diffusion is the predominant mass transfer mechanism. The mass transfer coefficient is then calculated from the Sherwood number given by:

$$Sh = \frac{kd_h}{D} = aRe^b Sc^c = f(Re, Sc, d_h) \tag{100}$$

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number, and d_h is the hydraulic diameter. For laminar tube flow the Sherwood number is

$$Sh = 1.62\left(ReSc\frac{d_h}{L}\right)^{1/3} \tag{101}$$

where L is the length of the tube. For turbulent tube flow it becomes

$$Sh = 0.04Re^{0.75}Sc^{1/3} \tag{102}$$

Here the product of the Reynolds and Schmidt numbers is known as the Péclet number, which is defined as

$$Pe \equiv \frac{\text{Convective fluid velocity}}{\text{Diffusive velocity}} = ReSc \tag{103}$$

The convective fluid velocity refers to the hydrodynamic fluid velocity outside the boundary layer that is parallel to the membrane surface. There are many useful empirical expressions of Sherwood numbers based on the entire membrane modules of hollow fibers in the literature [20-22].

3. Modified Péclet Number

Similar to the conventional Péclet number, the modified Péclet number can be used to study the mass transfer within the boundary layer using the convective velocity caused by the mass transfer instead of bulk fluid velocity [23]:

$$Pe^m \equiv \frac{\text{Convective velocity caused by mass transfer}}{\text{Diffusive velocity}} \tag{104}$$

From the basic mass flux expression, Eq. (5), the modified Péclet number can be written as

$$Pe^m \equiv \frac{v}{v_i - v} \tag{105}$$

Dividing Eq. (5) by the diffusion term, $c_i(v_i - v)$, we obtain

$$\frac{N_i}{J_i^*} = \frac{c_i v_i}{c_i(v_i - v)} = 1 + Pe^m \tag{106}$$

The left-hand side becomes

$$\frac{N_i}{J_i^*} = \frac{k(c_b - c_m)}{D(c_b - c_m)/\delta} = \frac{k\delta}{D} \tag{107}$$

Therefore Eq. (106) becomes

$$\frac{k\delta}{D} = 1 + Pe^m \tag{108}$$

This shows that the mass transfer coefficient is a simple linear function of a modified Péclet number in the boundary layer depicted in Fig. 6. When the modified Péclet number is 0 (diffusion dominant), the mass transfer coefficient becomes the same as D/δ. One

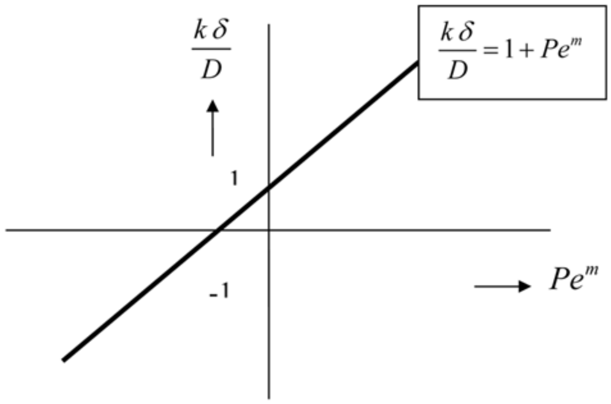

Fig. 6. Mass transfer coefficient versus modified Péclet number.

real-world example is the case of VOC pervaporation. If the modified Péclet number is −1, the mass transfer coefficient becomes 0. This is true in the boundary layer mass transfer of solute for RO, NF, UF, and MF.

Upon examination of the equations developed above, the following summarizes the boundary layer mass transfer for various membrane processes. For systems with very small and very large separation factors, $q\delta/D$ values are ln I and 0, respectively, as shown in Eqs. (95) and (96). When the separation factor becomes 1 (no separation), Eq. (95) indicates that $q\delta/D$ value approaches infinity. If the separation factor is less than 1, $q\delta/D$ value becomes positive, and if the separation factor is greater than 1, the $q\delta/D$ value becomes negative. The velocity of the permeating species of interest, v_1, can be compared to the average velocity, v, to assess the value of the modified Péclet number. When v_1 is 0, the value of the modified Péclet number becomes −1 as seen in Eq. (105). When $v_1=v$, the value of the modified Péclet number approaches infinity. When v_1 is much larger than v, the value of the modified Péclet number becomes 0. If v_1 is less or greater than v, the value of the modified Péclet number becomes less than −1 or greater than 0, respectively.

The above table covers the entire range of modified Péclet numbers except between −1 and 0. In this range the following conditions must be met for the modified Péclet number to be realizable: $-1<(v/(v_i-v))<0$, which can be re-expressed as $0<1+(v/(v_i-v))<1$, or it can be written as $0<(v/(v_i-v))<1$. The right side inequality states $v<0$, which means that the system must undergo a counter diffusion mass transfer. Therefore, it is impossible to have a modified Péclet number in the range of $-1<Pe^m<0$ for ordinary membrane permeation where all species are moving in the same direction.

TRANSPORT THROUGH THE MEMBRANE ITSELF

The transport process through the membrane itself varies according to the type of membrane used and the corresponding transport mechanism that occurs. Whether the membrane is made of polymeric or ceramic materials or whether it is porous or not will affect the transport mechanism and produce different flux equations.

1. Pore Model

When a membrane possesses pores, the permeating species favors the porous passage rather than going through the solid part. The size of the pores will determine which flow mechanism prevails: laminar, transition (slip flow), or Knudsen flow with surface diffusion. If the pores are equal to or smaller than the molecular sizes of the species, a molecular sieving mechanism may work. In such a case the activation diffusion model is suitable for describing the membrane transport.

1-1. Poiseuille (Laminar) and Knudsen (Free Molecular) Flow

When a majority of the gas molecules undergo intermolecular collisions rather than wall-to-wall collisions, a continuum regime and molecular chaos prevail. The equation of continuity holds and the flow of gases, F_p, can be described by the Poiseuille equation:

$$F_p = \frac{\pi r^4}{8\mu RT}\left(\frac{p_h + p_l}{2}\right)\left(\frac{p_h - p_l}{l}\right) \tag{109}$$

Here r is radius of the pore, μ is gas viscosity, R is the gas constant, and T is temperature. This continuum condition is met when the mean free path

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p} \tag{110}$$

is much smaller than the pore radius $\lambda \ll r$. Here, k is the Boltzmann constant, d is the collision diameter of gas molecules, and p is pressure.

In the reverse situation, when $\lambda \gg r$, the continuum concept breaks down and a rarefied gas condition will set in. This means that the intermolecular collisions become far less frequent compared to wall-to-wall collisions. This may happen even at a relatively high pressure. The molecular chaos then disappears and free molecular behavior rules. The flow rate of gas, F_{kn}, through such a fine pore obeys the Knudsen equation:

Table 1. Boundary layer mass transfer in various membrane separations

Membrane processes	Solute in RO, NF, UF, MF	Less permeable	No separation	More permeable	Pervaporation of VOC
A	≈ 0 [$1 \gg \alpha$]	$0<\alpha<1$	1	$1<\alpha$	∞ [$1 \ll \alpha$]
$Q\delta/D$	$\approx \ln I$	>0	∞	<0	≈ 0 [q/k]
q/k	$-\infty$	<0	0	$0<q/k<1/\alpha$	≈ 0 [$q\delta/D$]
$K\delta/D$	≈ 0	<0	∞	>1	≈ 1
v_1	$v_1 \approx 0$	$v_1<v$	$V_1=v$	$v<v_1$	$v \ll v_1$
Pe^m	≈ -1	<-1	∞	>0	≈ 0 [$(1+I)/2\alpha$]
K	≈ 0	<0	∞	$>D/\delta$	$\approx D/\delta$
I	>1	>1	1	$0<I<1$	$0<I^{**}<1$

** $I \approx 1-\alpha\, q/k$

$$F_{kn}=\frac{8\pi r^3}{3\sqrt{2\pi MRT}}\left(\frac{p_h-p_l}{l}\right) \tag{111}$$

Here, the molecular weight of gas, M, enters into the picture due to the free molecular nature of the flow regime.

If the mean free path is comparable to the pore radius, a transition from viscous flow to free molecular flow will occur. This is called slip flow, and the equation is

$$F_{sl}=\frac{\pi r^3}{2M\bar{v}}\left(\frac{p_h-p_l}{l}\right) \tag{112}$$

where the mean speed of gas molecules is given by

$$\bar{v}=\sqrt{\frac{8RT}{\pi M}} \tag{113}$$

All of the above equations are valid for a single cylindrical capillary, which represents a typical pore in the membrane. Additionally, these expressions are valid only for a pure species of gas. For real pores, some geometric parameters may enter into the equations, such as porosity and tortuosity.

For a mixture of gases, each component will obey its own equation separately for free molecular flow, thus yielding separation of species by membrane permeation. However, the separation factor is not large enough to be practical, because it is represented by the ratio of the inverse square root of the molecular weights. For a continuum, an average viscosity is used in the Poiseuille equation; therefore, no separation takes place in this regime of flow. Neither of the above flow mechanisms will result in much separation.

1-2. Surface Diffusion

If a membrane contains micropores, the interaction between the gas molecules and the pore walls cannot be neglected due to the large internal surface area. The adsorbed gas molecules on the pore walls can migrate through the porous membrane according to its gradient of surface concentration. This phenomenon, referred to as surface diffusion or surface flow, constitutes a significant portion of the gas permeation through a microporous membrane [24-32]. Fick's first law can be written for this two-dimensional diffusion:

$$F_s=D_s\left(\frac{C_{sh}-C_{sl}}{1}\right) \tag{114}$$

Here F_s is the surface diffusion flux, D_s is the surface diffusivity, and C_{sh} and C_{sl} represent the surface concentrations of the high pressure and low pressure sides, respectively. Based upon the local equilibrium concept, it has been shown that the surface diffusion can be combined with the Knudsen flow in parallel [31]:

$$F=F_{kn}+F_s \tag{115}$$

The amount of adsorption depends on pressure, temperature, and the interaction forces between the gas molecules and the pore walls. The amount of adsorption at a given temperature is expressed in terms of the adsorption isotherm. There are many adsorption isotherms ranging from monolayer to multilayer adsorption [33]. Consequently, the surface concentration can be expressed as a function of bulk phase (gas phase) pressure.

Based upon the statistical mechanical theory, the surface diffusivity and concentration can be treated as functions of the temperature and pressure in gas phase [27]. The overall permeability term is expressed as a function of temperature and pressure:

$$Q\sqrt{MT}=A+BTExp\left(\frac{\Delta}{T}\right) \tag{116}$$

Here A, B, and Δ are parameters that must be determined for a specific system. The constant A represents the Knudsen flow term, and the second term is the surface diffusion. The values of B and Δ correlate very well to the Lennard-Jones parameters, and in turn, to the critical properties [30]. The surface diffusion strongly depends on the gas-solid interactions. How closely a given gas-membrane system is depicted by a model interaction potential determines the accuracy of agreement between the experimental and theoretical permeabilities. However, these parameters of the interaction potentials between gases and membrane materials are not readily available.

Another approach is strongly based on the statistical mechanics using the Boltzmann equation [32]. Without making a distinction between the gas or surface phases, the total flow rate is calculated for gas molecules under a potential field in a narrow slit. The results show that the total flux increases considerably compared to a case without a potential field. This extra flow can be interpreted as the surface diffusion.

1-3. Activated Diffusion

When the pore size decreases in size and approaches molecular dimensions, the ordinary methods of determining surface diffusion encounter a difficulty: the pore spaces are so narrow that no clear-cut distinction can be made between the gas phase molecules, which are under a potential field and the surface adsorbed molecules. Since the pore walls are so close together, the interaction potentials overlap each other considerably [33,34], which creates a much stronger potential for the trapped gas molecules. As a result, the gas molecules are strongly attracted to these pores, but they must travel through the narrow and long passages. Since the interaction potential is so amplified, the gas molecules must overcome large activation energy barriers. This is the situation for zeolites or molecular sieves.

For such a membrane the predominant factor is the molecular size of the gases. For small molecules (or for large pores) with a weak interaction potential, the diffusivity is high. But for larger gas molecules (or for smaller pores) with a strong potential, the diffusivity decreases. In such a case the diffusivity depends primarily on the kinetic diameter of the gas [35]. The activated diffusion is treated much the same as the surface diffusion [36-38]. The diffusivity is expressed in an Arrhenius form as a function of an activation energy, E_a, and a pre-exponential factor, D_o:

$$D=D_o\left(-\frac{E_a}{RT}\right) \tag{117}$$

1-4. Capillary Condensation

When the interaction potential between gas molecules and pore walls becomes large, condensation may occur even before the thermodynamic saturation point is reached. This phenomenon is capillary condensation, and the lowered condensation pressure can be estimated by the Kelvin equation:

$$\frac{RT}{\rho}\ln\frac{p_t}{p_0}=-J\gamma+(p_t-p_0) \tag{118}$$

where ρ is the density of capillary condensate; p_t is the capillary condensation pressure, which is less than the saturated vapor pressure, p_0; J is the mean curvature; and γ is the surface tension. The capillary condensation occurs for any small pores to produce the high surface curvature of condensate whenever the pressure and temperature conditions are met within the pores.

When capillary condensation occurs, a tremendous capillary pressure can develop within pores, which then creates an added driving force. A suddenly increased flux is observed when this happens. Concurrently, if the pores are entirely filled with the condensate, the flow mechanism will follow the Poiseuille equation for a liquid. Altogether there are six different modes of flow, including surface diffusion and partial blockage of pores [39,40]. Another interesting aspect of capillary condensate flow involves a hysteresis in permeability measurements similar to the one in the adsorption-desorption cycle [40,41]. For newer membranes that contain smaller pores, the importance of the capillary condensation flow for gas separations is amplified [37,39-43]. When a mixture of condensable vapor and non-condensable gas flows through a microporous membrane, an infinite separation factor may be achieved due to the blockage of pores by the capillary condensate [43].

1-5. Dual-mode Sorption Model

According to the "dual-mode sorption" model [44-47], there are two types of sorptions that occur in a membrane: a Henry's law type and a Langmuir type of monolayer adsorption. The total adsorption, C_a, is given by a sum of the two:

$$C_a = C_d + C_h = k_d p + \frac{c_h' b p}{1+bp} \tag{119}$$

where the subscripts d and h denote the dense region (Henry's law region) and holes (Langmuir adsorption region), respectively, and k_d, c_h', and b are constants. The overall permeability is given by

$$Q = k_d D_d + \frac{c_h' b}{1+bp} D_h \tag{120}$$

where D_d and D_h represent the diffusivities for Henry and Langmuir types, respectively. Generally speaking, a glassy polymer consists of a dense region and micro-voids. The dense region is responsible for the Henry's law-type sorption, and the micro-voids (holes) possess the Langmuir adsorption sites.

1-6. Dusty-gas Model

As seen above, the gas transport mechanism varies widely depending on the structure, morphology, and materials of the membrane. The operating conditions, such as pressure and temperature, can also alter the flow scheme. A universal theory developed by Mason and his associates [48-51] simultaneously incorporates all of these mechanisms but is less used by the membrane community due to its complexity. This is called the "dusty-gas model." It encompasses even nonideal liquid transport as well as ordinary diffusion through a solid. A presentation of the equations will not be included here since they are rather involved; instead, the reader is referred to the above-mentioned references. Recently, Datta and coworkers [52] revisited this theory.

2. Solution-diffusion Model

The original theory of a solution-diffusion model was developed by Merten and his colleagues [53-56] and applied to a reverse osmosis system using a cellulose acetate membrane. Later, this model was adapted to many other membrane applications such as gas separation, pervaporation, and dialysis, and extended even to inorganic membrane materials. There are numerous review articles on this model in the literature, so only a brief summary is given here. According to this model, the overall permeability is a product of diffusivity and solubility of the permeating species in the membrane:

$$Q=DS \tag{121}$$

This equation is the essence of the solution-diffusion theory in membrane transport. The physical significance of this is that permeation depends not only on the kinetic property (diffusivity) but also on the equilibrium property (solubility). The permeating species must be dissolved in the membrane before it can diffuse through. Since both diffusivity and solubility follow approximately the Arrhenius type of temperature dependency, the permeability also roughly obeys the Arrhenius equation.

$$D = D_o\left(-\frac{E_D}{RT}\right) \text{ and } S = S_o\left(-\frac{E_S}{RT}\right) \tag{122}$$

Therefore setting $Q_o=D_oS_o$ and $E_Q=E_D+E_S$

$$Q = Q_o\left(-\frac{E_Q}{RT}\right) \tag{123}$$

3. Composite Membranes

For composite membranes the overall mass transfer resistance can vary, depending on the structure of the composite. If a simple lamination of multiple layers is used to construct a composite membrane such as a coated membrane, the total mass transfer resistance is the sum of the individual mass transfer resistances. However, if two or more different materials are mixed to produce a composite membrane (for example, adsorbent-filled polymer membrane) the overall permeability of the composite membrane can be calculated by using various model equations [57,58].

When two different materials are mixed to produce a composite membrane, the overall membrane properties can be derived from the individual properties of the constituent materials. The most common mixing rules are given below [58]:

$$Q=\phi Q_1+(1-\phi)Q_2 \tag{124}$$

where subscripts 1 and 2 represent the dispersed and continuous phases, respectively, and ϕ is the volume fraction of the dispersed phase. This equation is based upon the parallel flow concept, and therefore the composite permeability can be calculated using the parallel combination of individual mass transfer resistances.

For a series combination, a harmonic mean value of individual permeabilities is obtained:

$$\frac{1}{Q} = \frac{\phi}{Q_1} + \frac{1-\phi}{Q_2} \tag{125}$$

Assuming identical cubes of adsorbent particles are dispersed uniformly and isotropically throughout the polymer phase in a square lattice, the expression for the ratio of permeability of the filled membrane (Q) to that of the original polymer membrane (Q_2) is

$$\frac{Q}{Q_2} = \frac{1+\left(\frac{1}{\lambda}-1\right)(\phi^{1/3}-\phi)}{1+\left(\frac{1}{\lambda}-1\right)\phi^{1/3}} \tag{126}$$

where $l \equiv Q_1/Q_2$; Q_1 is the zeolite permeability and ϕ is the volume fraction of the dispersed phase (zeolite).

When the cubes are replaced with identical spheres of radius, the model yields

$$\frac{Q}{Q_2}=\frac{\pi z}{\left(\frac{1}{\lambda}-1\right)}-\frac{\pi}{2\left(\frac{1}{\lambda}-1\right)^2}\ln\left[2\left(\frac{1}{\lambda}-1\right)z+1\right]+1-\pi z \qquad (127)$$

where $z\equiv\left(\frac{3\phi}{4\pi}\right)^{1/3}$

For a heterogeneous medium a number of models have been developed, even including a tortuous diffusion path for the permeating species; there are several good summaries and comparisons among the different models [57,58]. Shape factors and tortuosity complicate models and produce different results. The problem of obtaining the overall composite property from the constituent's properties arises in other fields such as thermal conductivity, electrical conductivity, electrical or magnetic permittivity, dielectric constant, and elastic modulus.

4. Inorganic Membranes

Since the transport mechanisms in conventional porous inorganic membranes are well described by viscous flow, Knudsen flow, surface diffusion, capillary condensate flow, and molecular sieving flow, it will not be discussed here. Instead, very unusual flow mechanisms are outlined below to highlight the difference in their transport equations. These cases involve the gas permeations through certain metallic or ceramic membranes. The hydrogen flux J_{H_2} through a thick palladium membrane is known to obey [2]

$$J_{H_2}=Q_{H_2}\left(\frac{(P^u_{H_2})^{1/2}-(P^d_{H_2})^{1/2}}{l}\right) \qquad (128)$$

where l is the membrane thickness and Q_{H_2} is hydrogen permeability, which can be expressed as a product of diffusivity and solubility. The upstream and downstream partial pressures of hydrogen are $P^u_{H_2}$ and $P^d_{H_2}$, respectively. The square root dependency of flux on gas pressure is due to surface dissociation of the hydrogen molecule. However, the hydrogen permeation rate is generally determined by the surface exchange rates and the proton ion diffusion rate through the bulk membrane [4,5].

The oxygen permeation rate is generally determined by the surface exchange rates and the oxygen ion diffusion rate through the bulk membrane [6-11]. For a thick membrane, the surface exchange step may be ignored, and therefore the bulk diffusion is designated as the controlling rate. In this case, the oxygen permeation flux through oxygen ion-conducting ceramic membranes is expressed as

$$J_{O_2}=Q_{O_2}\left(\frac{(P^u_{O_2})^{-n}-(P^d_{O_2})^{-n}}{l}\right) \qquad (129)$$

where n is the power coefficient, which depends on the creation speed of oxygen vacancy with the change of ambient oxygen partial pressure; l is the membrane thickness: and Q_{O_2} is oxygen permeability, which can be expressed as a product of diffusivity and solubility. The upstream and downstream partial pressures of oxygen are $P^u_{O_2}$ and $P^d_{O_2}$, respectively. As the membrane thickness decreases, the oxygen permeation rate depends not only on the bulk diffusion, but also on the surface kinetics.

HOW DIFFERENT IS MEMBRANE MASS TRANSFER FROM OTHER MASS TRANSFER?

For many mass transfer systems the concentration gradient is the only driving force present. However, multiple driving forces may be evident in some membrane permeation systems such as gas separation and pressure-driven processes (RO, NF, UF, and MF). When multiple driving forces arise in membrane transport, the treatment of mass transfer analysis may have to be altered or extended to accommodate the additional driving forces properly. For example, the conventional definition of the mass transfer coefficient does not apply in the case illustrated below.

1. Definition of Mass Transfer Coefficient

If the concentration gradient is the only driving force, the mass transfer coefficient, k, is defined by the following flux equation:

$$N_i\equiv k(c_i^u-c_i^d) \qquad (130)$$

A more generalized definition is obtained by replacing the concentration with activity in the above equation. Since mass transfer takes place from high concentration to low concentration locations, the mass transfer coefficient is always positive for an ordinary mass transfer situation.

2. Multiple Driving Forces

As seen before in gas permeation and pressure-driven liquid processes such as RO, NF, UF, and MF, the pressure gradient is applied in addition to the concentration or osmotic pressure gradient. In these cases the simple flux equation given above (Eq. (130)) does not adequately describe the situation as shown in Eqs. (40) and (53), and therefore the mass transfer coefficient defined as above is not applicable. As a result, the method described in the previous section for estimating the mass transfer coefficient is useless in these cases.

3. Convective Mass Transfer (Perpendicular and Parallel Directions)

In many convective mass transfer problems, mass transfer is affected by the bulk motion of fluid. In that case the mass transfer coefficient in the boundary layer is estimated with the Sherwood number method as stated above. Here the bulk convective velocity is directed in parallel with the membrane surface. However, within the stagnant boundary layer near the membrane surface, the convective flow taking place outside this boundary layer is not directly relevant. Instead, the convective motion in the direction of mass transfer (direction of diffusion) is relevant for total permeation as shown in the total flux equation (Eq. (91)). It should be pointed out that the convection in bulk motion also indirectly influences the overall mass transfer by affecting the thickness the boundary layer. Therefore, in mass transfer the convective motions parallel and perpendicular to the membrane surface play important roles, while in all other transport phenomena only the parallel convective motion exists. This means that there is no analogy between the mass transfer and other transport phenomena with regard to the boundary layer convection. An extreme example is given below to illustrate this point.

4. Negative Mass Transfer Coefficient? (in Case of Concentration Polarization)

Consider the mass transfer of less permeable component within a boundary layer. In Fig. 3 it is evident that the less permeable species is accumulating near the membrane surface, yielding a higher concentration than that found in bulk. If a mass transfer coefficient is calculated based on Eq. (130), it becomes

$$k=\frac{N_i}{(c_i^u-c_i^d)}<0 \tag{131}$$

The denominator is negative due to the concentration buildup and the diffusion is directed in the opposite direction of total flux. The convective flux, the second term in Eq. (91), which is perpendicular to the membrane surface, is larger than the diffusion flux and thus the net total mass flux is still positive. The mass transfer coefficient thus becomes negative. This is absurd, but it is caused by forcing an invalid equation to yield the mass transfer coefficient. Eqs. (91) and (130) are not compatible with each other, and the mass transfer coefficient cannot be properly defined and used in this case. Additionally, the analogy between mass transfer coefficients and electrical resistance breaks down.

CONCLUSION

Membrane processes are new, additional chemical engineering operations that have many similarities to other equilibrium unit operations. However, they are all nonequilibrium processes, unlike conventional equilibrium processes. This fact is seldom emphasized in the literature. In the current review a generalized nonequilibrium thermodynamic analysis is given for all different membrane processes, including gas permeation, pervaporation, dialysis, reverse osmosis, ultrafiltration, nanofiltration, microfiltration, and electrodialysis. Starting from the entropy production term, fluxes and driving forces are identified for each membrane process and the linear expressions between fluxes and driving forces are presented with corresponding coefficients. It is possible to reduce these fluxes to conventional membrane transport equations. Consequently, flux equations are generalized to contain additional terms with additional driving forces that represent the coupling phenomena for all membrane processes.

Another unique aspect of membrane transport is the boundary layer mass transfer created by concentration polarization. The modified Péclet number is very useful and instructive for classifying and analyzing different types of membrane processes. With this approach, the limitation of using mass transfer coefficient is recognized for some membrane processes. If the definition of a conventional mass transfer coefficient is imposed, the value may become negative for the less permeable component in the boundary layer. This is due to the incompatibility of the two flux equations: the equation defining the mass transfer coefficient and the basic mass transfer equation in the boundary layer, which is the governing equation and includes diffusion and convection terms.

NOMENCLATURE

A : parameter
a : activity
B : parameter
b : constant
c : concentration
C : concentration
D : diffusion or dialysis coefficient
d : collision diameter of a molecule
d_h : hydraulic diameter
E : energy
F : flow rate or charge per mole of electrons=96,484.56
f : fugacity or function
G : Gibbs free energy
I : concentration polarization index or electric current
J : generalized flux or mean curvature
J_i^* : molar diffusion flux
K : overall mass transfer coefficient
k : Boltzmann constant
k_l : mass transfer coefficient in liquid boundary layer
k_m : mass transfer coefficient in membrane
L : phenomenological coefficient
l : membrane thickness
ln : natural logarithm
lmdel : log mean delta
M : molecular weight
N : molar mass flux with respect to stationary coordinates
P : pressure
p : pressure
$\overline{P}$: partial pressure
Pe : Péclet number
Q : permeability coefficient
q : heat or volume flux
R : gas constant
Re : Reynolds number
r : reflection coefficient or pore radius
S : entropy or solubility
Sc : Schmidt number
Sh : Sherwood number
T : absolute temperature
t : time
$\overline{V}$: partial molar volume
v : velocity vector; or molar average velocity
X : generalized driving force
x : mole fraction in liquid phase
y : mole fraction in gas phase
z : $(3\phi/4\pi)^{1/3}$
∇ : nabla (gradient)

Greek Letters

α : separation factor
γ : activity coefficient; or surface tension
Δ : difference; or a parameter
δ : boundary layer thickness
ζ : electric charge
λ : mean free path or ratio of permeabilities
μ : chemical potential; or shear viscosity
$\tilde{\mu}$: electrochemical potential
π : osmotic pressure
ρ : density
σ : rate of entropy generation
ϕ : electric potential or volume fraction
ω : solute permeability

Subscripts

a : activation

b : upstream bulk
D : diffusion or dialysis
d : dense region
E : energy
H_2 : hydrogen
h : Henry's law region or high
i : species
kn : Knudsen regime
l : low
m : at membrane surface
n : number of species
O_2 : oxygen
P : pressure driven
p : downstream bulk or Poiseuille regime
Q : permeation
S : solubility
s : solute (salt) or at surface
sl : slip regime
t : capillary condensation
V : volumetric
w : solvent (water)
o : constant

Superscripts

d : downstream
m : modified
s : saturated vapor
u : upstream
* : diffusion

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