Nonequilibrium Thermodynamics of Membrane Transport

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All membrane processes are nonequilibrium processes. The transport equation describing a particular membrane process must satisfy the principles of nonequilibrium thermodynamics. However, many expressions for the flux through a membrane as functions of the driving forces can be found in the literature without resorting to nonequilibrium thermodynamics. In fact, the choice of fluxes and driving forces for a particular membrane process frequently seems to be arbitrary and accidental; this is attributed to historical developments. Some exceptions are the cases of reverse osmosis and ultrafiltration processes. Katchalsky and coworkers successfully applied the principles of nonequilibrium thermodynamics by Onsager to analyze reverse osmosis and ultrafiltration processes. A generalized treatise of nonequilibrium thermodynamic analysis is given for all different membrane processes including gas permeation, pervaporation, dialysis, reverse osmosis, ultrafiltration, microfiltration, and electrodialysis. Starting from the entropy production term, fluxes and driving forces are ascertained for each membrane process and the linear expressions between fluxes and driving forces are presented with corresponding coefficients. These are identified with the conventional entities whenever possible. As a consequence of this treatment, flux equations are more generalized to contain additional terms with additional driving forces representing the coupling phenomena. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 862–870, 2004
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Introduction

All membrane permeation and separation processes are nonequilibrium processes unlike other unit operations of separation, such as distillation, extraction, and gas absorption, for example. The transport equation describing a particular membrane process must satisfy the principles of nonequilibrium thermodynamics. Katchalsky and Curran (1975) fully and successfully applied the nonequilibrium thermodynamic analysis for reverse osmosis and ultrafiltration processes. The choices of fluxes and driving forces and their transformations from one set to another have been also thoroughly investigated by Fitts (1962). However, for other membrane processes, it is not quite clear why a particular set of fluxes and driving forces is selected over other sets. Also, there seems to be a lack of generalized treatment of membrane transport equations in the literature except for special cases that will be referenced later in this article. It is therefore the objective of this article to present a generalized treatise of nonequilibrium thermodynamic analysis of transport equations for all different membrane processes including gas permeation, reverse osmosis, ultrafiltration, microfiltration, dialysis, electrodialysis, and pervaporation.

Theory

Flux equations

Consider a multicomponent membrane permeation process taking place across a membrane. A one-dimensional (1-D) problem can be treated without losing the essential aspect of thermodynamic expressions; this can then be generalized for a three-dimensional case if needed. At steady state, molar flux N_i

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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 with velocity v_i, which may be split into two terms as shown in Bird et al. (2002)

$$N_i \equiv c_i v_i = c_i(v_i - v^*) + c_i v^* \tag{1}$$

where c_i is molar concentration and v^* is the local molar average velocity defined by

$$v^* \equiv \frac{\sum_k c_k v_k}{\sum_k c_k} = \frac{\sum_k N_k}{\sum_k c_k} = \frac{N}{c} \tag{2}$$

where N and c are total molar flux and concentration, respectively. The molar flux relative to the molar average velocity can be identified as the diffusion flux J_i^*

$$J_i^* = c_i(v_i - v^*) = -D_i \frac{dc_i}{dz} \tag{3}$$

where D_i is diffusivity of i. The total flux is then the sum of diffusion flux and convection flux

$$N_i = J_i^* + \frac{c_i}{c} N = J_i^* + x_i(\text{or } y_i)N \tag{4}$$

where x_i and y_i are the mole fraction of i for liquid and gas phases, respectively.

When both sides of the above equation are summed up for all species

$$\sum_i N_i = \sum_i J_i^* + \sum_i x_i N \tag{5}$$

the following result is obtained that will play an important role in diffusion problems

$$\sum_i J_i^* = 0 \tag{6}$$

Nonequilibrium thermodynamic formalism

The principles of nonequilibrium thermodynamics originally proposed by Onsager (1931a,b) and later reformulated by Prigogine (1947, 1967), De Groot (1961), De Groot and Mazur (1962), Fitts (1962), Baranowski (1991), and Kondepudi and Prigogine (1998) state that the rate of lost work associated to entropy production per unit area due to any irreversible process is the scalar product (inner product) of steady state fluxes J_i and generalized forces X_i as shown below

$$T\sigma = \sum_i J_i X_i \tag{7}$$

Here T is the ambient temperature and σ is the rate of entropy production per unit area of membrane. The entropy production rate can be calculated from the entropy balance equation together with other balance equations of physical entities in question, such as mass, energy, and momentum, as shown in De Groot and Mazur (1962), Fitts (1962), and Kondepudi and Prigogine (1998). The split of fluxes and forces, however, is not always obvious or trivial; usually there can be many choices of different sets of fluxes and forces. It is also important to note that any arbitrary choices of fluxes and forces may not satisfy the Onsager relations given by Eq. 9 below; thus care must be exercised as discussed by Fitts (1962). This aspect is beyond the scope of the present article, and therefore will not be covered here.

The next principle says that these fluxes are linearly related to forces

$$J_i = \sum_k L_{ik} X_k \tag{8}$$

where L_{ij} are the phenomenological coefficients. These linear relationships indicate that any flux can be caused by any other driving forces in addition to its own conjugated force, which is the primary cause.

The phenomenological coefficients then satisfy the Onsager reciprocal relationships

$$L_{ik} = L_{ki} \tag{9}$$

The above three equations summarize all the principles of linear nonequilibrium thermodynamics for any irreversible processes, including membrane permeation. However, it should be pointed out that any particular choice of fluxes and forces is not unique. Many other equally valid choices are available as shown in the examples below.

Entropy production and lost work

The rate of lost work due to entropy production is a measure of the irreversibility associated with a given membrane process. Since Gibbs' free energy using the standard notations is

$$G = H - TS \tag{10}$$

then under any isothermal membrane transport process the lost work due to irreversible entropy production by ΔS can be expressed by

$$T\Delta S = \Delta H - \Delta G \tag{11}$$

Here the differences signify the changes across the membrane due to irreversibility. According to Prigogine (1947, 1967) and De Groot and Mazur (1962), total entropy change consists of external and internal contributions. In the present discussion, only the internal change due to irreversibility is relevant. From the first law of thermodynamics for an open system, it is evident that

$$\Delta H = 0 \tag{12}$$

for any membrane permeation process that can be considered as a Joule–Thompson process (with no significant heat transfer, no shaft work, no kinetic energy change, and no potential

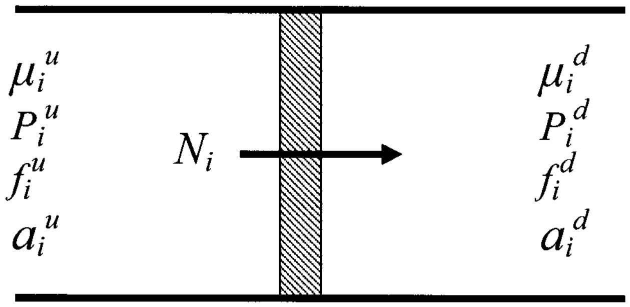

Figure 1. Steady-state membrane transport.

energy change). Thus, the lost work for any membrane process at a constant temperature can be expressed by the loss of Gibbs' free energy

$$T\Delta S = -\Delta G \tag{13}$$

If the rate of entropy production per unit area is σ, the rate of lost work is $T\sigma$, which must be the same as the rate of Gibbs' free energy loss attributed to membrane transport. Under a steady state, the following relationship is obtained in terms of molar flux N_i and chemical potential change $\Delta\mu_i$ across a membrane, as shown in Figure 1

$$T\sigma = -\Delta G = -\left[\sum_i N_i\mu_i^d - \sum_i N_i\mu_i^u\right] = -\sum_i N_i\Delta\mu_i \tag{14}$$

It should be noted here that the physical properties of fluid phases rather than membrane phase are used in the driving forces. The membrane is treated as a black box and does not participate in the entropy generation, just like the case of steady state heat conduction by a metal bar connected to high and low temperature sources.

Membrane permeation

To take advantage of equilibrium thermodynamic relationships of differential forms, a multicomponent membrane permeation process across an infinitesimally thin membrane must be considered. The chemical potential change across this thin membrane can be expressed in terms of the change in fugacity (or partial pressure) or activity of species i in fluid phase. Combined with the differential form of flux equation, the rate of entropy production will be obtained in a differential form first, then next in an integral expression. Starting with the Gibbs–Duhem equation

$$\sum_i x_i d\mu_i = -SdT + VdP \tag{15}$$

The following identity results for any isothermal membrane process

$$\sum_i x_i N d\mu_i = NVdP = qdP \tag{16}$$

where q is the total volumetric flux, which may not be a constant even for a steady state in general.

Using Eqs. 4 and 16 the following relationship is obtained

$$-\sum_i N_i d\mu_i = -\sum_i (J_i^* + x_i N)d\mu_i = -\sum_i J_i^* d\mu_i - NVdP \tag{17}$$

Therefore, the rate of lost work for any membrane process under a steady state can be expressed as

$$\begin{aligned} T\sigma &= -\sum_i N_i d\mu_i = -\sum_i N_i RTd(\ln f_i) \\ &= -\sum_i J_i^* d\mu_i - NVdP = -\sum_i J_i^* RTd(\ln f_i) - NVdP \end{aligned} \tag{18}$$

Any one of the expressions in Eq. 18 may be chosen to represent the rate of lost work during the membrane process of interest.

Now the first two expressions in Eq. 18 may be integrated readily for a finite membrane thickness from the fluid phase of one side of the membrane to the other side. At steady state N_i and J_i^* stay constant, thus the rate of lost work attributed to entropy production becomes

$$T\sigma = -\sum_i N_i\Delta\mu_i = -\sum_i N_i RT\Delta(\ln f_i) \tag{19}$$

The integrations of the second line in Eq. 18, however, should be carried out separately for gas and liquid phase operations due to the changing volume of gas phase.

In many of the membrane processes, the boundary layer mass transfer becomes an important issue; the discussion of concentration polarization requires this. Within the fluid phase (gas or liquid) of boundary layer, the same derivations will apply as in the membrane phase. Thus Eq. 18 would be valid within the boundary layer. The total volumetric flux q will be constant within the fluid phase

$$q = \sum_i N_i V_i = NV = \frac{N}{c} \tag{20}$$

By combining Eqs. 4 and 20, one obtains

$$N_i = J_i^* + c_i q \tag{21}$$

This celebrated Nernst–Planck equation is also useful within the boundary fluid layer for any membrane permeation process.

Ideal gas permeation

When a mixture of ideal gases is separated into two compartments by a permeable membrane and a pressure difference is applied across the membrane, gas permeation will take place as a consequence of the imbalance of the chemical potentials on two sides of the membrane. This irreversible process will cause an entropy production, according to Eq. 19. In using Eq. 19, all symbols are interpreted as those of bulk fluids. The second line in Eq. 18 can be now integrated for gas phase from upstream conditions to downstream conditions. Note that all fluxes remain constant under a steady state operation. Only the volume changes as a function of pressure. Using the ideal gas law, the integral form of the second line in Eq. 18 becomes

$$\begin{aligned} T\sigma &= -\sum_i J_i^* \Delta\mu_i - NRT\Delta(\ln P) \\ &= -\sum_i J_i^* RT\Delta(\ln f_i) - NRT\Delta(\ln P) \end{aligned} \tag{22}$$

By combining Eqs. 19 and 22 and replacing fugacity with partial pressure $\bar{P}$, the rate of lost work for ideal gas permeation can be rewritten as

$$\begin{aligned} T\sigma &= -\sum_i N_i \Delta\mu_i = -\sum_i N_i RT\Delta(\ln f_i) \\ &\approx -\sum_i N_i RT\Delta \ln \bar{P}_i = -\sum_i J_i^* RT\Delta(\ln y_i) - NRT\Delta(\ln P) \end{aligned} \tag{23}$$

As shown in the above equations, there can be many different choices of fluxes and forces to describe the gas permeation systems according to Eq. 7. The following example illustrates this.

Example 1: binary gas permeation

The first choice of fluxes and forces may be made for ideal gas permeation from the first expression in the top line of Eq. 23. Conforming this equation into the form of Eq. 7, the following relations are identified

$$J_1 = N_1 \tag{24}$$

$$J_2 = N_2 \tag{25}$$

$$X_1 = -\Delta\mu_1 \tag{26}$$

$$X_2 = -\Delta\mu_2 \tag{27}$$

The linear combinations of these fluxes and forces are given by Eq. 8

$$N_1 = L_{11}(-\Delta\mu_1) + L_{12}(-\Delta\mu_2) \tag{28}$$

$$N_2 = L_{21}(-\Delta\mu_1) + L_{22}(-\Delta\mu_2) \tag{29}$$

The above equations are the most general forms of gas permeation fluxes. However, the use of these equations in practical situations is very limited because the chemical potentials cannot be measured in the laboratory.

The second choice of fluxes and forces comes from the first expression of line two in Eq. 23

$$\begin{aligned} T\sigma &= -N_1 RT\Delta(\ln \bar{P}_1) - N_2 RT\Delta(\ln \bar{P}_2) \\ &= -N_1 RT \ln\left(\frac{\bar{P}_1^d}{\bar{P}_1^u}\right) - N_2 RT \ln\left(\frac{\bar{P}_2^d}{\bar{P}_2^u}\right) \end{aligned} \tag{30}$$

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

$$J_1 = N_1 \quad \text{and} \quad J_2 = N_2 \tag{31}$$

$$X_1 = -\frac{RT\Delta\bar{P}_1}{lmdel(\bar{P}_1)} \tag{32}$$

$$X_2 = -\frac{RT\Delta\bar{P}_2}{lmdel(\bar{P}_2)} \tag{33}$$

where the logarithmic mean values of partial pressures are introduced, which are defined by

$$lmdel(\bar{P}_1) \equiv \frac{\Delta\bar{P}_1}{\ln\left(\frac{\bar{P}_1^d}{\bar{P}_1^u}\right)} \tag{34}$$

$$lmdel(\bar{P}_2) \equiv \frac{\Delta\bar{P}_2}{\ln\left(\frac{\bar{P}_2^d}{\bar{P}_2^u}\right)} \tag{35}$$

The linear relationships between fluxes and forces are expressed as

$$N_1 = -L_{11}\frac{RT\Delta\bar{P}_1}{lmdel(\bar{P}_1)} - L_{12}\frac{RT\Delta\bar{P}_2}{lmdel(\bar{P}_2)} \tag{36}$$

$$N_2 = -L_{21}\frac{RT\Delta\bar{P}_1}{lmdel(\bar{P}_1)} - L_{22}\frac{RT\Delta\bar{P}_2}{lmdel(\bar{P}_2)} \tag{37}$$

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

$$N_1 = -Q_1\Delta\bar{P}_1 \tag{38}$$

$$N_2 = -Q_2\Delta\bar{P}_2 \tag{39}$$

with the following identifications of gas permeability coefficients

$$Q_1 \equiv L_{11}\frac{RT}{lmdel(\bar{P}_1)} \tag{40}$$

$$Q_2 \equiv L_{22}\frac{RT}{lmdel(\bar{P}_2)} \tag{41}$$

The third choice of fluxes and forces is made from the last expression of Eq. 23. Because of the nature of binary system, $J_1^* + J_2^*$, the first term in the last expression in Eq. 23 becomes

$$\sum_i J_i^* RT\Delta(\ln y_i) = J_1^* RT\Delta \ln(y_1/y_2) \tag{42}$$

Substituting Eq. 42 into Eq. 23 yields

$$\begin{aligned} T\sigma &= -NRT\Delta(\ln P) - J_1^* RT\Delta \ln(y_1/y_2) \\ &= -NRT\left(\ln \frac{P^d}{P^u}\right) - J_1^* RT\left(\ln \frac{y_1^d\, y_2^u}{y_1^u\, y_2^d}\right) \end{aligned} \tag{43}$$

The physical significance of the above equation is rather interesting. The first term in the second line represents the rate of lost work arising from the pressure expansion of an ideal gas and is always positive. The argument of logarithm of the second term is the separation factor. Because the separation factor is greater than one according to convention 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

$$N = L_{00}[-RT\Delta(\ln P)] + L_{01}[-RT\Delta \ln(y_1/y_2)] \tag{44}$$

$$J_1^* = L_{10}[-RT\Delta(\ln P)] + L_{11}[-RT\Delta \ln(y_1/y_2)] \tag{45}$$

Notice that in addition to the principal terms (the first term in Eq. 44 and second term in Eq. 45), which represent the conjugated phenomena, the cross terms (the other two terms) are also present in the total flux as well as in diffusion flux expressions. These cross terms represent the coupling phenomena that are predicted from the nonequilibrium thermodynamic theory. For many membrane processes, these coupling terms may be smaller than the principal (conjugated) terms, but they must be included. Specifically, the first term in Eq. 45 indicates that pressure diffusion may be present when diffusion takes place under a large pressure drop. Clearly, Eqs. 44 and 45 show that the coupling phenomenon is an important part of 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

$$N = -L_{00}RT\Delta(\ln P) \tag{46}$$

$$J_1^* = -L_{11}RT\Delta \ln(y_1/y_2) \tag{47}$$

The diffusion flux for the second species is not needed because it is identical to that for the first species with negative sign. As in the previous case, Eq. 46 can be easily identified with the conventional expression for total flux under a pressure drop with permeability coefficient (or filtration coefficient) as

$$Q_0 \equiv L_{00}\frac{RT}{lmdel(\bar{P})} \tag{48}$$

The expression for diffusion flux requires a little bit of transformation before it can be identified with the conventional formula. Making use of $y_1 + y_2 = 1$, Eq. 47 can be rewritten as

$$J_1^* = -L_{11}RT\left[\frac{1}{lmdel(y_1)} + \frac{1}{lmdel(y_2)}\right]\Delta y_1 = -D_1\Delta c_1 \tag{49}$$

where

$$D_1 \equiv \frac{L_{11}RT}{\bar{c}}\left[\frac{1}{lmdel(y_1)} + \frac{1}{lmdel(y_2)}\right] \tag{50}$$

It should be noted that Eq. 46 is for the total molar flux of binary gas mixture under a pressure drop. The driving force for diffusion in Eq. 47 is the separation factor, unlike the conventional case. This means that when there is no diffusion with gas permeation, there will be no separation. This fact has never been discussed in the literature.

The permeation flux equation given by Eq. 4 is a differential form. All variables in this equation are point functions at a 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. Substituting the diffusion and total flux expressions into Eq. 4 and using the average concentrations, the permeation flux for species i can be calculated by

$$N_i = J_i^* + \frac{\bar{c}_i}{\bar{c}}N = -D_i\Delta c_i - \frac{\bar{c}_i Q_0}{\bar{c}}\Delta P \tag{51}$$

The above equation will be very convenient in a case where a distinction needs to be made between different types of driving forces for gas permeation. For example, binary counterpermeation can take place in the absence of pressure drop across a membrane. The second term will drop out, leaving only the diffusion term. On the other hand, if a very porous (with large pores) membrane is placed between two chambers of different pressures, only the second term will be effective. This type of gas permeation gives no separation because no diffusion will take place and no concentration difference can be sustained. This happens for porous membrane filtration with very large pores.

As shown in the above discussions, three different entropy production expressions attributed to irreversibility, Eqs. 19, 30, and 43, can be made for the same permeation system; thus three different sets of fluxes and forces, Eqs. 28 and 29, 36 and 37, and 44 and 45, may be used to describe the same transport system of an ideal gas through a membrane. The nonuniqueness of entropy production rate expression gives freedom of choice in the selection of appropriate fluxes and forces. These flux equations show that coupling phenomena are possible in general for multicomponent gas transport through a membrane. However, not many couplings have been reported in the literature except for the pressure diffusion.

Liquid permeation (RO, UF, MF, dialysis, and so on)

Because most of liquid phases can be assumed to be incompressible, the last expression in Eq. 18 can be easily integrated from upstream side of the membrane to downstream side. At steady state J_i^* and the total volumetric flux, $q = NV$, stay constant; thus the rate of lost work attributed to entropy production is expressed as

$$\begin{aligned} T\sigma &= -\sum_i N_i RT\Delta(\ln f_i) = -\sum_i J_i^* RT\Delta(\ln f_i) - q\Delta P \\ &= -\sum_i J_i^* RT\Delta(\ln a_i) - q\Delta P \end{aligned} \tag{52}$$

The last expression in Eq. 52, the fugacity ratio, is replaced by the activity ratio using the definition of activity, $a_i \equiv f_i/f_i^o \equiv \gamma_i x_i$. All quantities represent those for the bulk phases on either side of the membrane.

Example 2: reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF)

For the sake of simplicity, this discussion will be 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, a part of the first term in the last expression in Eq. 52 for low solute concentration becomes

$$J_s^* RT\Delta(\ln a_s) \approx \frac{J_s^* RT\Delta(\gamma_s x_s)}{\gamma_s \bar{x}_s} \approx \frac{J_s^* RT\Delta x_s}{\bar{x}_s} \approx \frac{J_s^* RT\Delta c_s}{\bar{c}_s} = \frac{J_s^* \Delta\pi}{\bar{c}_s} \tag{53}$$

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

When the above equation is combined with the Gibbs–Duhem equation

$$\begin{aligned} RT\Delta(\ln a_w) &= -\frac{\bar{x}_s RT\Delta(\ln a_s)}{\bar{x}_w} \\ &\approx -\frac{RT\Delta x_s}{\bar{x}_w} \approx -\frac{RT\Delta c_s}{\bar{c}_w} = -\frac{\Delta\pi}{\bar{c}_w} \end{aligned} \tag{54}$$

With the substitution of Eqs. 53 and 54 into Eq. 52, the entropy production term now becomes

$$T\sigma = -\sum_i J_i^* RT\Delta(\ln a_i) - q\Delta P = -\frac{J_s^* \Delta\pi}{\bar{c}_s} + \frac{J_w^* \Delta\pi}{\bar{c}_w} - q\Delta P \tag{55}$$

A new flux can be defined as

$$J_D \equiv \frac{N_s}{\bar{c}_s} - \frac{N_w}{\bar{c}_w} = \frac{J_s^*}{\bar{c}_s} - \frac{J_w^*}{\bar{c}_w} \tag{56}$$

It should be noted that the above equation does not imply that the total flux is the same as the diffusion flux. The second equality results from the combined flux equations for salt and water, Eqs. 1 and 3. The flux defined by Eq. 56 is widely used in RO, UF, and MF, as shown originally by Katchalsky and Curran (1975).

The entropy production term becomes

$$T\sigma = -q\Delta P - J_D \Delta\pi \tag{57}$$

The linear flux equations are

$$-q = L_P \Delta P + L_{PD} \Delta\pi \tag{58}$$

$$-J_D = L_{DP} \Delta P + L_D \Delta\pi \tag{59}$$

These are the standard equations used in the field as derived by Katchalsky and Curran (1975).

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

$$r \equiv -\frac{L_{PD}}{L_P} \tag{60}$$

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

$$-q = L_P(\Delta P - r\Delta\pi) \tag{61}$$

This volume flux is used in conjunction with the following solute flux equation, which can be derived by combining Eqs. 56 through 61 and the definition of the following "solute permeability" that was derived by Katchalsky and Curran (1975)

$$\omega \equiv -\left(\frac{L_P L_D - L_{PD}^2}{L_P}\right)\bar{c}_s \tag{62}$$

$$N_s = \omega\Delta\pi + (1 - r)q\bar{c}_s \tag{63}$$

In the fields of reverse osmosis and ultrafiltration, the total volume flux from Eq. 61 and the solute flux from Eq. 63 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 (1975) and later demonstrated by Narebska and Kujawski (1994). When negligible osmotic pressure is present, as in some cases of ultrafiltration and microfiltration, only the total volume flux (Eq. 61) is needed with the filtration coefficient.

Through the above example, we can illustrate clearly how the nonuniqueness of splitting fluxes and forces and the importance of coupling phenomena manifest in nonequilibrium thermodynamics. The entropy production term for RO, UF, and MF expressed by Eqs. 14 and 57 can be further changed to reflect the latest transformations of fluxes and forces

$$T\sigma = -q(\Delta P - r\Delta\pi) - (rq + J_D)\Delta\pi \tag{64}$$

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, $(rq + J_D)$, is too cumbersome to be used in the laboratory, but it can be converted to yield the solute flux given by Eq. 63. Both of these are the result of coupling phenomena from Eqs. 58 and 59. The off-diagonal terms play the central role in RO, 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. 14, 57, and 64. Therefore the split of fluxes and forces is not unique. When the coupling terms are not present, the system degenerates to a trivial ordinary filtration and diffusion, and the essence of RO is completely missed.

Example 3: binary system of dialysis

The convenient starting place for a binary dialysis system is Eq. 52. Noting that there is no pressure drop applied for dialysis, Eq. 52 can be written as

$$T\sigma = J_1^* RT\Delta(\ln a_1) - J_2^* RT\Delta(\ln a_2) \tag{65}$$

Identifying the fluxes and forces with negligible convective contribution

$$J_1 = J_1^* \approx N_1 \tag{66}$$

$$J_2 = J_2^* \approx N_2 \tag{67}$$

$$X_1 = -RT\Delta \ln a_1 \tag{68}$$

$$X_2 = -RT\Delta \ln a_2 \tag{69}$$

The linear relationships between fluxes and forces are expressed as

$$N_1 \approx J_1^* = -L_{11}RT\Delta \ln a_1 - L_{12}RT\Delta \ln a_2 \tag{70}$$

$$N_2 \approx J_2^* = -L_{21}RT\Delta \ln a_1 - L_{22}RT\Delta \ln a_2 \tag{71}$$

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

$$N_1 = -D_{D1}\Delta c_1 \tag{72}$$

$$N_2 = -D_{D2}\Delta c_2 \tag{73}$$

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

$$D_{D1} \equiv \frac{L_{11}RT}{\bar{c}_1} \tag{74}$$

$$D_{D2} \equiv \frac{L_{22}RT}{\bar{c}_2} \tag{75}$$

Pervaporation

Pervaporation is a membrane separation process where the upstream side of the membrane is exposed to a liquid mixture, whereas the downstream side is in contact with a vapor phase of low pressure. When the difference of the chemical potential is taken, care must be exercised 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 vapor phase. The first expression in Eq. 23 can be written for the pervaporation process by assuming ideal gas law for vapor phase as

$$\begin{aligned} T\sigma &= -\sum_i N_i RT\Delta(\ln f_i) = -\sum_i N_i RT \ln(f_i^d/f_i^u) \\ &\approx -\sum_i N_i RT \ln\left(\frac{Py_i}{P_i^s \gamma_i x_i}\right) \end{aligned} \tag{76}$$

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

Example 4: binary pervaporation

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

$$T\sigma = -\sum_i N_i RT\Delta(\ln f_i) \approx -\sum_i N_i RT \ln\left(\frac{Py_i}{P_i^s \gamma_i x_i}\right) = \sum_i J_i X_i \tag{77}$$

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

$$J_s = N_s \quad \text{and} \quad J_w = N_w \tag{78}$$

$$X_s \equiv -\frac{RT\Delta f_s}{lmdel(f_s)} \tag{79}$$

$$X_w \equiv -\frac{RT\Delta f_w}{lmdel(f_w)} \tag{80}$$

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

$$-\Delta f_s = f_s^u - f_s^d = P_s^s \gamma_s x_s - Py_s \tag{81}$$

$$-\Delta f_w = f_w^u - f_w^d = P_w^s \gamma_w x_w - Py_w \tag{82}$$

The logarithmic mean delta values are defined as before:

$$lmdel(f_s) \equiv \frac{\Delta f_s}{\ln \dfrac{f_s^d}{f_s^u}} \tag{83}$$

$$lmdel(f_w) \equiv \frac{\Delta f_w}{\ln \frac{f_w^d}{f_w^u}} \tag{84}$$

The linear relationships between fluxes and forces are expressed as

$$N_s = -L_{11}\frac{RT\Delta f_s}{lmdel(f_s)} - L_{12}\frac{RT\Delta f_w}{lmdel(f_w)} \tag{85}$$

$$N_w = -L_{21}\frac{RT\Delta f_s}{lmdel(f_s)} - L_{22}\frac{RT\Delta f_w}{lmdel(f_w)} \tag{86}$$

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

$$N_s = Q_s(P_s^s\gamma_s x_s - Py_s) \tag{87}$$

$$N_w = Q_w(P_w^s\gamma_w x_w - Py_w) \tag{88}$$

where two permeabilities for solute and solvent are defined by

$$Q_s \equiv -L_{11}\frac{RT}{lmdel(f_s)} \tag{89}$$

$$Q_w \equiv -L_{22}\frac{RT}{lmdel(f_w)} \tag{90}$$

In the pervaporation field, Eqs. 87 and 88 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 (1989).

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 total driving force is an electrochemical potential difference that includes the electromotive potential difference without pressure drop. The electrochemical potential $\tilde{\mu}$ for a species i with a charge of ζ_i under an external electric potential ϕ is defined as

$$\tilde{\mu}_i \equiv \mu_i + \zeta_i F\phi \tag{91}$$

where F is the charge per mole of electrons ($F = 96{,}484.56$). The lost work attributed to electrodialysis can be expressed from Eq. 52 with this modification

$$T\sigma = -\sum_i N_i\Delta\tilde{\mu}_i = -\sum_i N_i(\Delta\mu_i + \zeta_i F\Delta\phi_i) \tag{92}$$

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, ascribed to the electrical interaction. The linear flux equations can thus be written as below, ignoring all off-diagonal terms and the convective term

$$N_i \approx J_i^* = -L_{ii}(RT\Delta \ln a_i + \zeta_i F\Delta\phi_i) \tag{93}$$

$$N_i \approx J_i^* = -D_{Di}\left(\Delta c_i + \frac{\zeta_i F}{RT}\Delta\phi_i\right) \tag{94}$$

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

$$D_{Di} \equiv \frac{L_{ii}RT}{\bar{c}_i} \tag{95}$$

The hydraulic pressure difference plays little role in electrodialysis. Equation 94 is used to describe the permeation flux in electrodialysis, as shown by Hwang and Kammermeyer (1975).

There are many other phenomena dealing with membrane transport as discussed by De Groot (1961), De Groot and Mazur (1962), Fitts (1962), and Kondepudi and Prigogine (1998), which are omitted here for the sake of brevity. Nonequilibrium thermodynamics of electrokinetic effects across mixed-lipid membranes is reported by Rizvi and Zaidi (1986). Transport through charged membranes was studied by Narebska et al. (1985, 1987a,b, 1995a,b, 1997).

Conclusions

The unified treatment of nonequilibrium thermodynamics yields conventional flux equations with appropriate driving forces for every specific membrane process. The key is to express the chemical potential in terms of more convenient variables for the particular membrane process under consideration. The appropriate choice of fluxes and forces becomes important when it appears ambivalent in the entropy production expression. In principle all choices are equally valid as long as they satisfy Onsager's reciprocal relationships, although some are more convenient in practice for dealing with experimental data than others. It should be emphasized here that the nonuniqueness of the choices of fluxes and forces plays an important role. A general guideline is shown in the present article how one can initially describe a given membrane process from a theoretical standpoint and relate to experimentally observable quantities. Also shown is how the particular driving forces can be used and justified for a certain membrane process.

Unlike the conventional flux equations, the flux equations derived in the present analysis show the coupling phenomena. The magnitudes of these terms may be smaller than the principal (conjugated) terms; nevertheless, the nonequilibrium theory shows that they have to be included in general. In the case of binary gas permeation, as shown in Eqs. 44 and 45, the cross terms (coupling phenomena) are present in the total flux as well as in diffusion flux expressions. Specifically, the pressure diffusion term is predicted by the first term in Eq. 45. For the system of RO, UF, MF, dialysis, and pervaporation, similar coupling phenomena can be observed in their flux equations, as shown in Eqs. 58, 59, 70, 71, 85, and 86. The reflection coefficient defined by Eq. 60 is a measure of coupling that plays an important role in these processes. In the case of electrodialysis, more complex coupling terms could be present, but they are omitted here for the sake of simplicity.

In all cases, when the coupling terms are ignored, these general flux equations reduce to the conventional flux equations that are used in those particular fields. The general theory of nonequilibrium thermodynamics thus offers a unified approach to any membrane processes and the flux equations contain possible coupling terms.

Notation

a = activity
c = concentration
D = diffusion coefficient
F = Faraday constant
f = fugacity
G = Gibbs' free energy
H = enthalpy
i = species
J = generalized flux
J^* = diffusion flux
L = phenomenological coefficient
lmdel = log mean delta defined by Eq. 46
N = total flux with respect to stationary coordinates
P = pressure
$\bar{P}$ = partial pressure
Q = permeability coefficient
q = volume flux
R = gas constant
r = reflection coefficient
S = entropy
T = absolute temperature
V = volume
v = velocity
v^* = molar average velocity
X = generalized driving force
x = mole fraction
y = mole fraction in gas phase
z = spatial coordinate in the direction of mass transfer

Greek letters

Δ = difference between upstream and downstream
ϕ = electric potential
γ = activity coefficient
μ = chemical potential
$\tilde{\mu}$ = electrochemical potential
π = osmotic pressure
σ = rate of entropy production
ζ = number of electric charge
$\bar{\ }$ = average
ω = solute permeability

Superscripts

$*$ = diffusion
d = downstream
u = upstream
s = saturated vapor

Subscripts

D = dialysis
i, k, l = species
s = solute
w = solvent

Literature Cited

Baranowski, B., "Non-equilibrium Thermodynamics as Applied to Membrane Transport," *J. Membr. Sci.*, **57**, 119 (1991).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, **p.** 537 (2002).

De Groot, S. R., *Introduction to Thermodynamics of Irreversible Processes*, North Holland, Amsterdam, p. 94 (1961).

De Groot, S. R., and P. Mazur, *Non-Equilibrium Thermodynamics*, Interscience Publishers, New York, p. 20 (1962).

Fitts, D. D., *Nonequilibrium Thermodynamics*, McGraw-Hill, New York, p. 9 (1962).

Hwang, S. T., and K. Kammermeyer, *Membranes in Separations*, Wiley, New York, p. 204 (1975).

Katchalsky, A. and P. F. Curran, *Nonequilibrium Thermodynamics*, Harvard University Press, Cambridge, MA, p. 113 (1975).

Kedem, O., "The Role of Coupling in Pervaporation," *J. Membr. Sci.*, **47**, 277 (1989).

Kondepudi, D., and I. Prigogine, *Modern Thermodynamics*, Wiley, New York, p. 344 (1998).

Narebska, A., and S. Koter, "Irreversible Thermodynamics of Transport across Charged Membranes, Part III," *J. Membr. Sci.*, **30**, 141 (1987b).

Narebska, A., and S. Koter, "Irreversible Thermodynamics of Transport across Charged Membranes. A Comparative Treatment," *Polish J. Chem.*, **71**, 1643 (1997).

Narebska, A., S. Koter, and W. Kujawski, "Irreversible Thermodynamics of Transport Across Charged Membranes, Part I," *J. Membr. Sci.*, **25**, 153 (1985).

Narebska, A., S. Koter, A. Warzawski, and T. T. Le, "Irreversible Thermodynamics of Transport across Charged Membranes, Part VI," *J. Membr. Sci.*, **106**, 39 (1995b).

Narebska, A., and W. Kujawski, "Diffusion Dialysis—Transport Phenomena by Irreversible Thermodynamics," *J. Membr. Sci.*, **88**, 167 (1994).

Narebska, A., W. Kujawski, and S. Koter, "Irreversible Thermodynamics of Transport across Charged Membranes, Part II," *J. Membr. Sci.*, **30**, 125 (1987a).

Narebska, A., A. Warzawski, S. Koter, and T. T. Le, "Irreversible Thermodynamics of Transport across Charged Membranes, Part V," *J. Membr. Sci.*, **106**, 25 (1995a).

Onsager, L., "Reciprocal Relations in Irreversible Processes I," *Phys. Rev.*, **37**, 405 (1931a).

Onsager, L., "Reciprocal Relations in Irreversible Processes II," *Phys. Rev.*, **38**, 2265 (1931b).

Prigogine, I., *Etude Thermodynamique des Prosseus Irreversibles*, Desoer, Liege (1947).

Prigogine, I., *Introduction to Thermodynamics of Irreversible Processes*, Wiley, New York, p. 40 (1967).

Rizvi, S. A., and S. B. Zaidi, "Nonequilibrium Thermodynamics of Electrokinetic Effects across Mixed-Lipid Membranes," *J. Membr. Sci.*, **29**, 259 (1986).

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