Ambiguity and Non-uniqueness in Nonequilibrium Thermodynamics

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Abstract−The ambiguity and non-uniqueness of splitting fluxes and forces from the entropy generation equation raise confusion in nonequilibrium thermodynamics and misunderstanding of the Onsager reciprocal relationships. However, they provide an opportunity to select different sets of fluxes and forces that represent a given nonequilibrium process. By symmetrization of the phenomenological coefficient matrix, one can always find a proper set of fluxes and forces. This paper shows how the implementation of the transformation theory can produce several different sets of fluxes and forces through many engineering examples such as ideal gas permeation through a membrane, reverse osmosis, nanofiltration, ultrafiltration, and simultaneous heat and mass transfer. Also, guidance is presented on how to study nonequilibrium thermodynamics for a given irreversible process together with a short summary of the principles of nonequilibrium thermodynamics. These contain the entropy generation equation, linear relations of fluxes and all generalized forces including the Curie theorem, and the Onsager reciprocal relationships.

Key words: Nonequilibrium Thermodynamics, Reciprocal Relations, Transformation of Fluxes and Forces, Membrane Transport, Coupling Phenomena

INTRODUCTION

The linear theory of nonequilibrium thermodynamics (NT) has been very successful in explaining various coupling phenomena and generalizing the flux equations in terms of all available driving forces in many fields. The basic principles of NT were 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]. Katchalsky and Curran [1975] successfully applied the NT analysis for reverse osmosis and ultrafiltration processes, and Narebska and Kujawski [1994] also demonstrated that their experimental data fit the theory in dialysis processes. Kedem [1989] emphasized the role of coupling phenomenon in the application of NT to pervaporation of alcohol and water. Many other transport phenomena are discussed by de Groot [1961], de Groot and Mazur [1962], Fitts [1962], and Kondepudi and Prigogine [1998], but are omitted here for the sake of brevity. Rizvi and Zaidi [1986] reported NT of electrokinetic effects across mixed-lipid membranes. Narebska et al. [1985, 1987a, b, 1994, 1997, 1995a, b, 1997] studied transport through charged membranes.

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, electric charge, and momentum, as demonstrated in the books by de Groot and Mazur [1962], Fitts [1962], and Kondepudi and Prigogine [1998]. According to Prigogine [1947, 1967] and de Groot and Mazur [1962], the total entropy change consists of external and internal contributions. In the discussion of NT, only the internal change due to irreversibility is relevant. The split of fluxes and forces, however, is not always obvious or trivial; usually there can be many different sets of fluxes

and forces representing equally well the system under study. It is also important to note that any arbitrary choices of fluxes and forces may not satisfy the Onsager relations, especially when a magnetic field is present. Thus care must be exercised as discussed by de Groot and Mazur [1962] and Fitts [1962]. This aspect is beyond the scope of the present paper, and therefore it is not covered here.

The ambiguity and non-uniqueness of splitting fluxes and forces from the entropy generation equation may appear to be shortcomings of NT. However, we can take advantage of this aspect and use it more profitably by transforming a given set of fluxes and forces into another set that could produce more useful forms in explaining laboratory data. Therefore, it is the main goal of this paper to illustrate how one can accomplish such a task by taking a number of examples occurring in engineering.

PRINCIPLES OF NONEQUILIBRIUM THERMODYNAMICS

There are only a few principles or hypotheses that are the fundamental basis of NT. The phenomenological theory of NT concerns physicochemical changes taking place at the macroscopic level under a steady state near equilibrium. The approach of classical equilibrium thermodynamics is to calculate the changes in thermodynamic functions between two equilibrium states. In NT, these changes are directly dealt with in terms of fluxes and generalized forces. The development of NT formalisms by Onsager [1931a, b] is generally accepted as the linear theory of NT.

1. Local Equilibrium

Although the system considered in this paper is undergoing nonequilibrium processes overall, every small volume element in the system is assumed to have every thermodynamic state variable (equilibrium property), such as temperature, pressure, internal energy, entropy, etc.

2. Entropy Generation

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According to the second law of thermodynamics, any nonequilibrium process must accompany an entropy generation. In NT, the rate of entropy generation is a scalar (inner or dot) product of all fluxes (steady state) and all forces. In the analysis of NT, this hypothesis is usually the starting point. The entropy generation for a given process can be obtained from the balance equations of all transport entities such as mass, momentum, energy, electric charge, and entropy of the system as shown by de Groot and Mazur [1962], Fitts [1962], and Kondepudi and Prigogine [1998]. It is simple and elegant to use the algebraic notation, but the same content can be expressed by using index notation if one prefers.

$$T\sigma = \mathbf{J}^T \mathbf{X} \tag{1}$$

or $T\sigma = \sum_i J_i X_i$

Here, σ is the rate of entropy generation per unit volume, T is the system temperature, $\mathbf{J}$ represents all fluxes, and $\mathbf{X}$ represents all generalized forces. The superscript ^{T} indicates transposed quantity. The fluxes and forces may be tensorial entities of any rank in general. For example, chemical reactions are scalars, heat and mass transfers are vectors, and second rank tensors represent the momentum transfers, etc. However, the entropy generation rate must always be a scalar quantity for all processes. In the present paper, the product notation without any symbol between $\mathbf{J}^T$ and $\mathbf{X}$ in the above equation means a scalar (inner or dot) product between all conjugated fluxes and forces. Since the entropy generation rate σ in Eq. (1) must be positive definite, the scalar product between fluxes and forces for any irreversible process must be also positive definite. If it becomes zero, the process must be reversible according to the second law of thermodynamics.

3. Linear Relations between Fluxes and Forces

The next hypothesis in NT is that all fluxes are linearly related to all forces in the near-equilibrium linear regime. This postulate is a very powerful one, because it allows the possibility of coupling phenomena when multiple fluxes and forces are involved.

$$\mathbf{J} = \mathbf{L}\,\mathbf{X} \tag{2}$$

or $J_i = \sum_j L_{ij} X_j$

where $\mathbf{L}$ is a phenomenological coefficient tensor. There are some restrictions on this hypothesis for isotropic systems, which will be discussed in the following section on Curie's theorem.

4. Curie's Theorem

Some authors (de Groot and Mazur [1962], Kondepudi and Prigogine [1998]) call this the Curie symmetry principle. The most general form of this theorem states "fluxes and forces of different tensorial character do not couple for an isotropic system." Some examples of different tensorial characters are the following: scalars, polar (true) vectors, axial vectors (anti-symmetric tensors), isotropic tensors, and deviatoric (polar) tensors that are symmetric tensors with zero trace. The proof is omitted here as it is rather simple and can be found in de Groot and Mazur [1962].

5. Onsager Reciprocal Relations and Coupling

The last hypothesis in NT is that the phenomenological coefficients that appear in flux equations are symmetric, as proposed by Onsager [1931a, b].

$$\mathbf{L} = \mathbf{L}^T \tag{3}$$

or $L_{ij} = L_{ji}$

A slight modification of Eq. (3) is needed when there is a magnetic field present as described by Fitts [1962] and de Groot and Mazur [1962]. This principle plays the central role in NT. The off-diagonal components represent various coupling phenomena. Because of the reciprocal relations, there is a tremendous economy in the number of experimental measurements. At the macroscopic level, this principle of symmetry (reciprocal relations) is generally treated as a postulate, while in statistical thermodynamics it can be derived based on the microscopic reversibility, as originally shown by Onsager [1931a, b]. Since it is postulated, it has to be experimentally verified for a given irreversible process whenever a new set of fluxes and forces are employed. However, it is not necessary to do so if one can find a transformation from a set of fluxes and forces satisfying the Onsager reciprocal relations to another set that satisfies all three postulates as discussed below.

In summary, the only hypotheses needed in NT are the assumptions of local equilibrium and Eqs. (1), (2), and (3). Furthermore, it should be emphasized here that the choice of fluxes and forces is not unique, and there are many other useful choices that are more convenient for a given irreversible process as discussed below.

TRANSFORMATION OF FLUXES AND FORCES

1. Symmetrization of the Phenomenological Coefficient Matrix

Suppose we have a set of fluxes and forces expressing the irreversible system at hand that satisfies Eqs. (1) and (2), but not (3). In other words, when the Onsager reciprocal relations are not satisfied for a chosen set of fluxes and forces, we can transform this set into a proper set of fluxes and forces that will satisfy all three postulates (Eqs. (1), (2), and (3)) by defining the new phenomenological coefficients as follows:

$$\mathbf{L}' = \tfrac{1}{2}(\mathbf{L} + \mathbf{L}^T) = (\mathbf{L}')^T \tag{4}$$

If the old forces are kept unchanged, the new fluxes will become:

$$\mathbf{J}' = \mathbf{L}'\mathbf{X} \tag{5}$$

The scalar (inner) product between fluxes and forces will then be:

$$(\mathbf{J}')^T\mathbf{X} = \mathbf{X}^T(\mathbf{L}')^T\mathbf{X} = \tfrac{1}{2}\mathbf{X}^T(\mathbf{L}^T+\mathbf{L})\mathbf{X} = \tfrac{1}{2}\mathbf{J}^T\mathbf{X} + \tfrac{1}{2}\mathbf{X}^T\mathbf{J} = T\sigma \tag{6}$$

Thus this transformation gives a new set of fluxes $\mathbf{J}'$ and forces $\mathbf{X}' = \mathbf{X}$, which satisfies all three equations of NT.

Another way of looking at this problem is initially to assume a non-symmetric phenomenological coefficient for a chosen set of fluxes and forces. If the coefficient is decomposed into two parts--one for symmetric and another for anti-symmetric components--the flux equation would then be:

$$\mathbf{J} = \mathbf{LX} = \tfrac{1}{2}(\mathbf{L}+\mathbf{L}^T)\mathbf{X} + \tfrac{1}{2}(\mathbf{L}-\mathbf{L}^T)\mathbf{X} \tag{7}$$

If the above split is used to make a scalar (inner) product between the fluxes and forces,

$$\begin{aligned}\mathbf{J}^T\mathbf{X} &= \tfrac{1}{2}\mathbf{X}^T(\mathbf{L}+\mathbf{L}^T)\mathbf{X} + \tfrac{1}{2}\mathbf{X}^T(\mathbf{L}-\mathbf{L}^T)\mathbf{X}\\ &= \tfrac{1}{2}\mathbf{X}^T\mathbf{J} + \tfrac{1}{2}\mathbf{J}^T\mathbf{X} + \tfrac{1}{2}\mathbf{X}^T\mathbf{J} - \tfrac{1}{2}\mathbf{J}^T\mathbf{X} = T\sigma\end{aligned} \tag{8}$$

It is clear that the anti-symmetric part can be described as:

$$\tfrac{1}{2}\mathbf{X}^T(\mathbf{L}-\mathbf{L}^T)\mathbf{X} = \tfrac{1}{2}\mathbf{X}^T\mathbf{J} - \tfrac{1}{2}\mathbf{J}^T\mathbf{X} = 0 \tag{9}$$

Therefore we see from Eqs. (8) and (9) that the contribution of the anti-symmetric part (the second half of the flux in Eq. (8)) to the entropy generation term is zero. This means that the second part of the flux (with the anti-symmetric phenomenological coefficient) can happen only for a reversible process. For any irreversible process, the scalar product between fluxes and forces must be positive definite according to the second law of thermodynamics. This fact suggests that we can construct a proper set of fluxes and forces by transforming the initial fluxes into a new set of fluxes with only symmetric phenomenological coefficients and by keeping the old forces. Thereby, a new set of fluxes and forces can be made that satisfies all three principles of NT and upholds the Onsager reciprocal relationships. However, this is not automatically guaranteed when the initial set of fluxes and forces is chosen arbitrarily.

2. Invariant Transformation

Consider a linear transformation from a proper set of fluxes and forces into another set through a transformation matrix $\mathbf{T}$ as shown below:

$$\mathbf{J}' = \mathbf{TJ} \tag{10}$$

$$\mathbf{X}' = (\mathbf{T}^T)^{-1}\mathbf{X} \tag{11}$$

The scalar product between the new fluxes and forces becomes:

$$(\mathbf{J}')^T\mathbf{X}' = (\mathbf{TJ})^T(\mathbf{T}^T)^{-1}\mathbf{X} = \mathbf{J}^T\mathbf{T}^T(\mathbf{T}^T)^{-1}\mathbf{X} = \mathbf{J}^T\mathbf{X} = T\sigma \tag{12}$$

This leaves the entropy generation term unchanged. Substituting Eq. (2) into Eq. (10), we obtain:

$$\mathbf{J}' = \mathbf{T}(\mathbf{LX}) = \mathbf{TLT}^T(\mathbf{T}^T)^{-1}\mathbf{X} = \mathbf{L}'\mathbf{X}' \tag{13}$$

where $\mathbf{L}' = \mathbf{TLT}^T = (\mathbf{L}')^T$ \hfill (14)

Thus, we know that this particular transformation satisfies the format of Eqs. (1), (2), and (3). It should be noted that Eq. (12) leaves the entropy generation term intact without changing its value, while Eqs. (13) and (14) maintain only the formality. Therefore, the new expressions by a set of new fluxes $\mathbf{J}'$ and forces $\mathbf{X}'$ with a newly defined phenomenological coefficient $\mathbf{L}'$ still describe the same physical system. This means there is a great deal of flexibility in the selection of transformation matrix $\mathbf{T}$ that will produce a new proper set of fluxes and forces. Many examples of this type of linear transformation in NT are given by de Groot [1961] and Fitts [1962].

3. Symmetry of Fluxes and Forces

An even more outrageous view (or interpretation) of symmetry involves switching of the fluxes and forces while still satisfying Eqs. (1), (2), and (3). Transposing Eq. (1), we obtain:

$$T\sigma = (\mathbf{J}^T\mathbf{X})^T = \mathbf{X}^T\mathbf{J} \tag{15}$$

This equation is exactly the same form as Eq. (1), with the interpretation of "flux" $\mathbf{X}$ and "force" $\mathbf{J}$. From Eq. (2), we obtain:

$$\mathbf{X} = \mathbf{L}^{-1}\mathbf{J} \tag{16}$$

This shows that the new fluxes are a linear combination of the new forces with the phenomenological coefficient matrix $\mathbf{L}^{-1}$ (in a variant form of Eq. (2)). When Eq. (3) is inverted, the following equation is obtained:

$$(\mathbf{L})^{-1} = (\mathbf{L}^T)^{-1} = \mathbf{L}^{-1} = (\mathbf{L}^{-1})^T \tag{17}$$

This proves that the new phenomenological coefficients satisfy the Onsager reciprocal relationship.

4. Ambiguity and Non-uniqueness

When we start with the entropy generation expression, Eq. (1), and split the fluxes and forces to write Eq. (2), there are no guidelines provided by NT theory. This ambiguity and non-uniqueness of fluxes and forces for a given irreversible process can cause considerable confusion for a beginner. However, this is the beauty of the symmetry of NT. This also means there is the freedom of choice and flexibility in expression of the phenomena when using NT formalism. As shown in the symmetrization transformation, we can always choose a proper set of fluxes and forces. We can later find other sets of fluxes and forces that might better describe the system or be appropriate for correlation of experimental measurements through the invariant transformation.

EXAMPLES

1. Ideal Gas Permeation through Membrane

When a gas mixture permeates through a membrane under a steady state, the rate of lost work due to the irreversibility is the rate of lost free energy as shown by Hwang [2004]:

$$T\sigma = -\sum_i N_i d\mu_i = -\sum_i N_i RT d(\ln f_i) \tag{18}$$

Here, N_i is the molar flux of species i, $d\mu_i$ is the chemical potential difference for species i across an infinitesimal membrane element, R is the gas constant, and f_i is the fugacity of species i. We can confine our discussion to a binary system and use the differential driving force without the loss of its generality. For an ideal binary gas mixture, the above equation can be expressed as:

$$T\sigma = -N_1 RT d(\ln \overline{P}_1) - N_2 RT d(\ln \overline{P}_2) \tag{19}$$

We have replaced the fugacities with partial pressures $\overline{P}_1, \overline{P}_2$ for an ideal gas. The flux equations may be written as:

$$N_1 = L_{11}(-RT d\ln \overline{P}_1) + L_{12}(-RT d\ln \overline{P}_2) \tag{20}$$

$$N_2 = L_{21}(-RT d\ln \overline{P}_1) + L_{22}(-RT d\ln \overline{P}_2) \tag{21}$$

Therefore the following identifications result:

$$J_1 = N_1 \tag{22}$$

$$J_2 = N_2 \tag{23}$$

$$X_1 = -RT d\ln \overline{P}_1 \tag{24}$$

$$X_2 = -RT d\ln \overline{P}_2 \tag{25}$$

Now we can transform these fluxes and forces into a new set of fluxes and forces using the transformation matrix $\mathbf{T}$ according to Eqs. (10) and (11) as follows:

$$\mathbf{T} = \begin{pmatrix} y_2 & -y_1 \\ 1 & 1 \end{pmatrix} \tag{26}$$

$$\mathbf{J}' = \mathbf{TJ} = \begin{pmatrix} y_2 & -y_1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \begin{pmatrix} y_2 N_1 - y_1 N_2 \\ N_1 + N_2 \end{pmatrix} = \begin{pmatrix} J_1^* \\ N \end{pmatrix} \tag{27}$$

where y_1 and y_2 are the mole fractions of species 1 and 2. The last expression utilizes the relationships $N = N_1 + N_2$ and $N_1 = J_1^* + y_1 N$ as

defined by Bird et al. [2002].

$$\mathbf{X}' = (\mathbf{T}^T)^{-1}\mathbf{X} = \begin{pmatrix} 1 & -1 \\ y_1 & y_2 \end{pmatrix}\begin{pmatrix} -RTd\ln\overline{P}_1 \\ -RTd\ln\overline{P}_2 \end{pmatrix}$$
$$= \begin{pmatrix} -RTd\ln\overline{P}_1 + RTd\ln\overline{P}_2 \\ -y_1 RTd\ln\overline{P}_1 - y_2 RTd\ln\overline{P}_2 \end{pmatrix} \quad (28)$$

Since $\overline{P}_1 = Py_1$ and $\overline{P}_2 = Py_2$,

$$\mathbf{X}' = \begin{pmatrix} -RTd\ln(y_1/y_2) \\ -RTd\ln P \end{pmatrix} \quad (29)$$

The new phenomenological coefficients are:

$$\mathbf{L}' = \mathbf{TLT}^T = \begin{pmatrix} y_2 & -y_1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix}\begin{pmatrix} y_2 & 1 \\ -y_1 & 1 \end{pmatrix} \quad (30)$$

The newly transformed fluxes and forces are related by:

$$\mathbf{J}' = \mathbf{L}'\mathbf{X}' \quad (31)$$

The substitution of Eqs. (27) and (29) into Eq. (31) results in:

$$\begin{pmatrix} J_1^* \\ N \end{pmatrix} = \begin{pmatrix} L_{11}' & L_{12}' \\ L_{21}' & L_{22}' \end{pmatrix}\begin{pmatrix} -RTd\ln(y_1/y_2) \\ -RTd\ln P \end{pmatrix} \quad (32)$$

This is exactly the same expression obtained previously by Hwang [2004].

2. Reverse Osmosis (RO), Nanofiltration (NF), and Ultrafiltration (UF)

For liquid phase membrane transport, we start with the same entropy generation expression as in the gas phase transport according to Eq. (18) as shown by Hwang [2004].

$$T\sigma = -\sum_i N_i d\mu_i \quad (33)$$

We will use an example for a binary system again, where subscripts s and w represent solute (salt) and solvent (water), respectively. The fluxes and forces are identified:

$$J_1 = N_w \quad (34)$$

$$J_2 = N_s \quad (35)$$

$$X_1 = -d\mu_w \quad (36)$$

$$X_2 = -d\mu_s \quad (37)$$

The flux equations are:

$$\mathbf{J} = \mathbf{LX} = \begin{pmatrix} N_w \\ N_s \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix}\begin{pmatrix} -d\mu_w \\ -d\mu_s \end{pmatrix} \quad (38)$$

Next we transform the above set of fluxes and forces into a new set of fluxes and forces by a transformation matrix $\mathbf{T}$:

$$\mathbf{T} = \begin{pmatrix} \overline{V}_w & \overline{V}_s \\ -\dfrac{1}{c_w} & \dfrac{1}{c_s} \end{pmatrix} \quad (39)$$

where $\overline{V}_w$ and $\overline{V}_s$ are the partial molar volumes and c_w and c_s are

the molar concentration of solvent and solute, respectively. The new flux expression becomes:

$$\mathbf{J}' = \mathbf{TJ} = \begin{pmatrix} \overline{V}_w & \overline{V}_s \\ -\dfrac{1}{c_w} & \dfrac{1}{c_s} \end{pmatrix}\begin{pmatrix} N_w \\ N_s \end{pmatrix} = \begin{pmatrix} \overline{V}_w N_w + \overline{V}_s N_s \\ -\dfrac{N_w}{c_w} + \dfrac{N_s}{c_s} \end{pmatrix} \quad (40)$$

If the well-recognized total volumetric flux, J_V, and the diffusion flux J_D as described by Katchalsky and Curran [1975],

$$J_V = \overline{V}_w N_w + \overline{V}_s N_s \quad (41)$$

$$J_D = \dfrac{N_s}{c_s} - \dfrac{N_w}{c_w} \quad (42)$$

are used, Eq. (40) can be re-expressed as:

$$\mathbf{J}' = \begin{pmatrix} J_V \\ J_D \end{pmatrix} \quad (43)$$

The method outlined above can then be used to find the new forces with the transformation matrix $\mathbf{T}$. However, it is much simpler to use an approximate $\mathbf{T}$ without compromising the accuracy in cognizance of the usual approximation for a dilute solution:

$$\overline{V}_w N_w \gg \overline{V}_s N_s \cong 0, \quad \dfrac{1}{c_w} \cong \overline{V}_w, \quad J_V \cong \overline{V}_w N_w \quad (44)$$

Then the approximated $\mathbf{T}$ becomes:

$$\mathbf{T} = \begin{pmatrix} \overline{V}_w & 0 \\ -\dfrac{1}{c_w} & \dfrac{1}{c_s} \end{pmatrix} \quad (45)$$

If this approximate transformation matrix is applied, the following equation results:

$$\mathbf{J}' = \mathbf{TJ} = \begin{pmatrix} \overline{V}_w & 0 \\ -\dfrac{1}{c_w} & \dfrac{1}{c_s} \end{pmatrix}\begin{pmatrix} N_w \\ N_s \end{pmatrix} = \begin{pmatrix} \overline{V}_w N_w \\ -\dfrac{N_w}{c_w} + \dfrac{N_s}{c_s} \end{pmatrix} = \begin{pmatrix} J_V \\ J_D \end{pmatrix} \quad (46)$$

We can transform the forces using this approximate matrix:

$$\mathbf{T}^T = \begin{pmatrix} \overline{V}_w & -\dfrac{1}{c_w} \\ 0 & \dfrac{1}{c_s} \end{pmatrix} \quad (47)$$

$$(\mathbf{T}^T)^{-1} = \begin{pmatrix} \dfrac{1}{\overline{V}_w} & c_s \\ 0 & c_s \end{pmatrix} \quad (48)$$

$$\mathbf{X}' = (\mathbf{T}^T)^{-1}\mathbf{X} = \begin{pmatrix} \dfrac{1}{\overline{V}_w} & c_s \\ 0 & c_s \end{pmatrix}\begin{pmatrix} -d\mu_w \\ -d\mu_s \end{pmatrix} = \begin{pmatrix} -\dfrac{d\mu_w}{\overline{V}_w} - c_s d\mu_s \\ -c_s d\mu_s \end{pmatrix} = \begin{pmatrix} -dP \\ -d\pi \end{pmatrix} \quad (49)$$

Katchalsky and Curran [1975] derived the well-known identities in the last step of the above equation.

$$d\mu_w = \overline{V}_w(dP - d\pi) \tag{50}$$

$$d\mu_s = \frac{d\pi}{c_s} \tag{51}$$

The new phenomenological coefficients can be found by using:

$$\mathbf{L}' = \mathbf{TLT}^T = \begin{pmatrix} \overline{V}_w & 0 \\ -\dfrac{1}{c_w} & \dfrac{1}{c_s} \end{pmatrix} \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \overline{V}_w & -\dfrac{1}{c_w} \\ 0 & \dfrac{1}{c_s} \end{pmatrix} \tag{52}$$

The new flux expressions are:

$$\begin{pmatrix} J_V \\ J_D \end{pmatrix} = \begin{pmatrix} L_P & L_{PD} \\ L_{DP} & L_D \end{pmatrix} \begin{pmatrix} -dP \\ -d\pi \end{pmatrix} \tag{53}$$

The above equations are well established in the RO, NF, and UF fields, as shown in Katchalsky and Curran [1975]. The entropy generation expression remains invariant:

$$T\sigma = -N_w d\mu_w - N_s d\mu_s$$
$$= -J_V dP - J_D d\pi \tag{54}$$

The Onsager reciprocal relationship also remains valid in the new set of fluxes and forces.

Here is another transformation from the above transformed set. Consider a transformation matrix $\mathbf{S}$:

$$\mathbf{S} = \begin{pmatrix} 1 & 0 \\ r & 1 \end{pmatrix} \tag{55}$$

where the conventional definition of reflection coefficient is used:

$$r = -\frac{L_{PD}}{L_P} = -\frac{L_{DP}}{L_P} \tag{56}$$

The second part in the above equation is due to the Onsager reciprocal relationship. The reflection coefficient is an excellent example of the coupling phenomenon. The coupling between the osmotic pressure and the hydraulic pressure is a major phenomenon in RO, NF, and UF, unlike in many other cases where the conjugated terms dominate and the coupling (cross) terms are quite small. The transformed new fluxes become:

$$\mathbf{J}'' = \mathbf{SJ}' = \begin{pmatrix} 1 & 0 \\ r & 1 \end{pmatrix} \begin{pmatrix} J_V \\ J_D \end{pmatrix} = \begin{pmatrix} J_V \\ rJ_V + J_D \end{pmatrix} \tag{57}$$

The transposed inverse of $\mathbf{S}$ is found by using

$$(\mathbf{S}^T)^{-1} = \begin{pmatrix} 1 & -r \\ 0 & 1 \end{pmatrix} \tag{58}$$

and the new forces are:

$$\mathbf{X}'' = (\mathbf{S}^T)^{-1}\mathbf{X}' = \begin{pmatrix} 1 & -r \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -dP \\ -d\pi \end{pmatrix} = \begin{pmatrix} -dP + rd\pi \\ -d\pi \end{pmatrix} \tag{59}$$

The transformed phenomenological coefficient matrix is:

$$\mathbf{L}'' = \mathbf{SL}'\mathbf{S}^T = \begin{pmatrix} 1 & 0 \\ -\dfrac{L_{PD}}{L_P} & 1 \end{pmatrix} \begin{pmatrix} L_P & L_{PD} \\ L_{DP} & L_D \end{pmatrix} \begin{pmatrix} 1 & -\dfrac{L_{PD}}{L_P} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} L_P & 0 \\ 0 & L_D - \dfrac{L_{PD}^2}{L_P} \end{pmatrix} \tag{60}$$

The last expression of the above equation shows that it is a diagonal form of a matrix. Thus it can be said that formally the fluxes and forces have been diagonalized without any coupling effects. A similar diagonalization was achieved by de Groot [1961]. The new fluxes and forces are related as follows:

$$\begin{pmatrix} J_V \\ rJ_V + J_D \end{pmatrix} = \begin{pmatrix} L_P & 0 \\ 0 & L_D - \dfrac{L_{PD}^2}{L_P} \end{pmatrix} \begin{pmatrix} -dP + rd\pi \\ -d\pi \end{pmatrix}$$
$$= \begin{pmatrix} -L_P(dP - rd\pi) \\ -\left(L_D - \dfrac{L_{PD}^2}{L_P}\right)d\pi \end{pmatrix} \tag{61}$$

The new set of fluxes and forces is aesthetically pleasing, but a slight rearrangement yields a more practical flux equation for the second component:

$$rJ_V + J_D = -\frac{\omega}{c_s}d\pi \tag{62}$$

where $\omega = \left(L_D - \dfrac{L_{PD}^2}{L_P}\right)c_s \tag{63}$

The above quantity ω is known as "solute permeability." Using Eq. (46), the following expression is obtained:

$$J_V + J_D = \overline{V}_w N_w + \left(\frac{N_s}{c_s} - \frac{N_w}{c_w}\right)$$
$$= \frac{N_s}{c_s} = (1-r)J_V - \frac{\omega}{c_s}d\pi \tag{64}$$

From the last expression in the above equation, the solute flux equation is obtained:

$$N_s = (1-r)c_s J_V - \omega d\pi \tag{65}$$

This equation, together with the total volume flux,

$$J_V = -L_P(dP - rd\pi) \tag{66}$$

describes the same system just as well as the previous flux equations. All three sets of fluxes and forces are discussed by Katchalsky and Curran [1975]. However, for the first time it is shown in the current work that those sets of fluxes and forces can be interconverted by using the transformation theory. There are three parameters associated with these equations that characterize a given pressure-driven process (RO, NF, or UF): the hydraulic permeability L_P, the solute permeability through membrane ω, and the reflection coefficient r. This new description is widely employed in the RO, NF, and UF fields, and these three parameter values are measured experimentally. As stated before, the importance of the coupling term in this case (the second term in Eq. (66)) is so great that it may become the focal point of study, unlike the other irreversible processes where the coupling terms are usually very small in comparison to the conjugated terms.

As we have seen in the above examples, the split of fluxes and forces from the entropy generation expression is not unique and there can be many equivalent sets of fluxes and forces that satisfy all three NT principles (Eqs. (1), (2), and (3)). It is therefore up to the individual investigator to choose which set of fluxes and forces are suitable and most convenient. We can thus state that NT is not only useful, but also very instructional. It provides a means that can

lead to a practical set of fluxes and forces if the original set was not very helpful in the laboratory.

3. Simultaneous Heat and Mass Transfer

Fitts [1962] and de Groot [1961] calculated the lost energy due to entropy generation for a system where heat conduction and diffusion take place simultaneously:

$$T\sigma = -\left(q + \sum_i N_i \overline{H}_i\right) d\ln T - \sum_i N_i Td\left(\frac{\mu_i}{T}\right) \tag{67}$$

where q is heat flux and $\overline{H}_i$ is partial molar enthalpy of species i. Thus the fluxes and forces are:

$$\mathbf{J} = \begin{pmatrix} -J_E \\ N_1 \\ N_2 \\ \vdots \\ N_n \end{pmatrix} \tag{68}$$

where $J_E = q + \sum_i N_i \overline{H}_i$ (69)

This represents the energy flux for this system as a sum of heat flux by conduction and the energy carried by mass fluxes.

$$\mathbf{X} = \begin{pmatrix} d\ln T \\ -Td\left(\frac{\mu_1}{T}\right) \\ -Td\left(\frac{\mu_2}{T}\right) \\ \vdots \\ -Td\left(\frac{\mu_n}{T}\right) \end{pmatrix} \tag{70}$$

The flux equation is $\mathbf{J} = \mathbf{LX}$, which can be written with its components as:

$$-J_E = L_{00}d\ln T - L_{01}Td\left(\frac{\mu_1}{T}\right) - L_{02}Td\left(\frac{\mu_2}{T}\right) \cdots - L_{0n}Td\left(\frac{\mu_n}{T}\right)$$

$$N_1 = L_{10}d\ln T - L_{11}Td\left(\frac{\mu_1}{T}\right) - L_{12}Td\left(\frac{\mu_2}{T}\right) \cdots - L_{1n}Td\left(\frac{\mu_n}{T}\right)$$

$$N_2 = L_{20}d\ln T - L_{21}Td\left(\frac{\mu_1}{T}\right) - L_{22}Td\left(\frac{\mu_2}{T}\right) \cdots - L_{2n}Td\left(\frac{\mu_n}{T}\right) \tag{71}$$

$$\vdots$$

$$N_n = L_{n0}d\ln T - L_{n1}Td\left(\frac{\mu_1}{T}\right) - L_{n2}Td\left(\frac{\mu_2}{T}\right) \cdots - L_{nn}Td\left(\frac{\mu_n}{T}\right)$$

where $\mathbf{L} = \mathbf{L}^T$ is phenomenological coefficient matrix.

There are many other equally good choices of fluxes and forces available to describe this system. Consider a linear transformation by a transformation matrix $\mathbf{T}$:

$$\mathbf{T} = \begin{pmatrix} 1 & \mu_1 & \mu_2 \cdots \mu_n \\ 0 & 1 & 0 \cdots 0 \\ 0 & 0 & 1 \cdots 0 \\ \vdots & & \\ 0 & 0 & \cdots\cdots 1 \end{pmatrix} \tag{72}$$

so that the new fluxes $\mathbf{J}'$ become:

$$\mathbf{J}' = \mathbf{TJ} = \begin{pmatrix} 1 & \mu_1 & \mu_2 \cdots \mu_n \\ 0 & 1 & 0 \cdots 0 \\ 0 & 0 & 1 \cdots 0 \\ \vdots & & \\ 0 & 0 & \cdots\cdots 1 \end{pmatrix} \begin{pmatrix} -J_E \\ N_1 \\ N_2 \\ \vdots \\ N_n \end{pmatrix} = \begin{pmatrix} J'_0 \\ J'_1 \\ J'_2 \\ \vdots \\ J'_n \end{pmatrix} \tag{73}$$

where $\mathbf{J}'_0 = -J_E + \sum_i N_i \mu_i = -q - \sum_i N_i(\overline{H}_i - \mu_i) = -\left(q + \sum_i N_i T\overline{S}_i\right)$ (74)

and $J'_i = N_i$; for all i, $1 \le i \le n$ (75)

where $\overline{S}_i$ is the partial molar entropy for species i.

Now we find $(\mathbf{T}^T)^{-1}$

$$(\mathbf{T}^T)^{-1} = \begin{pmatrix} 1 & 0 & \cdots\cdots 0 \\ -\mu_1 & 1 & 0 \cdots 0 \\ -\mu_2 & 0 & 1 \cdots 0 \\ \vdots & & \\ -\mu_n & 0 & \cdots\cdots 1 \end{pmatrix} \tag{76}$$

so that we can transform the forces by $\mathbf{X}' = (\mathbf{T}^T)^{-1}\mathbf{X}$ as shown below.

$$\mathbf{X}' = \begin{pmatrix} 1 & 0 & \cdots\cdots 0 \\ -\mu_1 & 1 & 0 \cdots 0 \\ -\mu_2 & 0 & 1 \cdots 0 \\ \vdots & & \\ -\mu_n & 0 & \cdots\cdots 1 \end{pmatrix} \begin{pmatrix} d\ln T \\ -Td\left(\frac{\mu_1}{T}\right) \\ -Td\left(\frac{\mu_2}{T}\right) \\ \vdots \\ -Td\left(\frac{\mu_n}{T}\right) \end{pmatrix}$$

$$= \begin{pmatrix} d\ln T \\ -\mu_1 d\ln T - Td\left(\frac{\mu_1}{T}\right) \\ -\mu_2 d\ln T - Td\left(\frac{\mu_2}{T}\right) \\ \vdots \\ -\mu_n d\ln T - Td\left(\frac{\mu_n}{T}\right) \end{pmatrix} = \begin{pmatrix} d\ln T \\ -d\mu_1 \\ -d\mu_2 \\ \vdots \\ -d\mu_n \end{pmatrix} \tag{77}$$

The new flux equation $\mathbf{J}' = \mathbf{L}'\mathbf{X}'$ becomes:

$$\begin{pmatrix} J'_0 \\ J'_1 \\ J'_2 \\ \vdots \\ J'_n \end{pmatrix} = \begin{pmatrix} L'_{00} & L'_{01} & L'_{02} \cdots L'_{0n} \\ L'_{10} & L'_{11} & L'_{12} \cdots L'_{1n} \\ L'_{20} & L'_{21} & L'_{22} \cdots L'_{2n} \\ \vdots & & \\ L'_{n0} & L'_{n1} & L'_{n2} \cdots L'_{nn} \end{pmatrix} \begin{pmatrix} d\ln T \\ -d\mu_1 \\ -d\mu_2 \\ \vdots \\ -d\mu_n \end{pmatrix} \tag{78}$$

with the definitions of fluxes given by Eqs. (73) and (74). All off-diagonal components represent coupling between heat flow and mass flow, such as thermal diffusion (Soret effect) and the Dufour effect. The entropy generation term can be rewritten as $T\sigma = \mathbf{J}^T\mathbf{X} = \mathbf{J}'^T\mathbf{X}'$ using Eqs. (74), (75), (77), and (78):

$$T\sigma = -\left(q + \sum_i N_i T\overline{S}_i\right) d\ln T - \sum_i N_i d\mu_i \tag{79}$$

The physical significance of this expression is that when heat and mass transfer take place under temperature and chemical potential gradients, the total energy flux is the sum of heat flux (due to pure conduction) and the energy dissipation by the entropy flux carried by mass fluxes. This makes sense because the total entropy generation consists of energy dissipations due to heat conduction and mass transfer, and the entropy flux carried by mass fluxes.

Now consider the second transformation effected by matrix $\mathbf{S}$ on the original set of fluxes and forces:

$$\mathbf{S} = \begin{pmatrix} 1 & \overline{H}_1 & \overline{H}_2 \cdots \overline{H}_n \\ 0 & 1 & 0 \cdots 0 \\ 0 & 0 & 1 \cdots 0 \\ \vdots & & \\ 0 & 0 & \cdots \cdots 1 \end{pmatrix} \tag{80}$$

$$\mathbf{J}'' = \mathbf{S}\mathbf{J} = \begin{pmatrix} 1 & \overline{H}_1 & \overline{H}_2 \cdots \overline{H}_n \\ 0 & 1 & 0 \cdots 0 \\ 0 & 0 & 1 \cdots 0 \\ \vdots & & \\ 0 & 0 & \cdots \cdots 1 \end{pmatrix} \begin{pmatrix} -J_E \\ N_1 \\ N_2 \\ \vdots \\ N_n \end{pmatrix} = \begin{pmatrix} J_0'' \\ J_1'' \\ J_2'' \\ \vdots \\ J_n'' \end{pmatrix} \tag{81}$$

where $J_0'' = -J_E + \sum_i N_i \overline{H}_i = -q$ (82)

and $J_i'' = N_i$; for all i, $1 \le i \le n$ (83)

Now we find $(\mathbf{S}^T)^{-1}$:

$$(\mathbf{S}^T)^{-1} = \begin{pmatrix} 1 & 0 & \cdots \cdots 0 \\ -\overline{H}_1 & 1 & 0 \cdots 0 \\ -\overline{H}_2 & 0 & 1 \cdots 0 \\ \vdots & & \\ -\overline{H}_n & 0 & \cdots \cdots 1 \end{pmatrix} \tag{84}$$

so that we can transform the forces by $\mathbf{X}'' = (\mathbf{S}^T)^{-1}\mathbf{X}$ as shown below.

$$\mathbf{X}'' = \begin{pmatrix} X_0'' \\ X_1'' \\ X_2'' \\ \vdots \\ X_n'' \end{pmatrix} = \begin{pmatrix} 1 & 0 & \cdots \cdots 0 \\ -\overline{H}_1 & 1 & 0 \cdots 0 \\ -\overline{H}_2 & 0 & 1 \cdots 0 \\ \vdots & & \\ -\overline{H}_n & 0 & \cdots \cdots 1 \end{pmatrix} \begin{pmatrix} d\ln T \\ -Td\left(\dfrac{\mu_1}{T}\right) \\ -Td\left(\dfrac{\mu_2}{T}\right) \\ \vdots \\ -Td\left(\dfrac{\mu_n}{T}\right) \end{pmatrix} \tag{85}$$

where $X_0'' = d\ln T$ (86)

and $X_i'' = -\overline{H}_i d\ln T - Td\left(\dfrac{\mu_i}{T}\right) = (\mu_i - \overline{H}_i)d\ln T - d\mu_i$

$= -T\overline{S}_i d\ln T - d\mu_i = -d_T\mu_i$; for all i, $1 \le i \le n$ (87)

In the last expression in the above equation, $d_T\mu_i$ represents the isothermal change of the chemical potential. A similar notation was employed by Fitts [1962]. The newly transformed fluxes are linearly related to these forces by $\mathbf{J}'' = \mathbf{L}''\mathbf{X}''$ as follows:

$$\begin{pmatrix} -q \\ N_1 \\ N_2 \\ \vdots \\ N_n \end{pmatrix} = \begin{pmatrix} L_{00}'' & L_{01}'' & L_{02}'' & \cdots & L_{0n}'' \\ L_{10}'' & L_{11}'' & L_{12}'' & \cdots & L_{1n}'' \\ L_{20}'' & L_{21}'' & L_{22}'' & \cdots & L_{2n}'' \\ \vdots & & & & \\ L_{n0}'' & L_{n1}'' & L_{n2}'' & \cdots & L_{nn}'' \end{pmatrix} \begin{pmatrix} d\ln T \\ -d_T\mu_1 \\ -d_T\mu_2 \\ \vdots \\ -d_T\mu_n \end{pmatrix} \tag{88}$$

The entropy generation term can be rewritten as $T\sigma = \mathbf{J}^T\mathbf{X} = \mathbf{J}''^T\mathbf{X}''$ by using Eqs. (82), (83), (86), and (87):

$$T\sigma = -qd\ln T - \sum_i N_i d_T\mu_i \tag{89}$$

It should be emphasized here that all three entropy generation expressions, Eqs. (67), (79), and (89), give not only the same formalism (scalar product of fluxes and forces), but also the same value. All three sets of fluxes and forces satisfy all three fundamental principles of NT, Eqs. (1), (2), and (3). They equally represent the irreversible process under consideration. The ambiguity of splitting the entropy generation term or the non-uniqueness of choosing fluxes and forces offers great deal of freedom in describing a given NT system. Therefore, we may take advantage of this uncertainty or non-uniqueness to our benefits by using NT.

4. Stress Tensor for Newtonian Fluid (Example of Curie's Theorem)

The momentum transport equations involve second rank tensors. Our illustration will be confined to only isotropic Newtonian fluids. The viscous dissipation that represents the internal entropy generation due to momentum transport is $-\boldsymbol{\tau}:\nabla v$ as discussed by de Groot and Mazur [1962], Fitts [1962], and Bird et al. [2002]. Here $\boldsymbol{\tau}$ is the stress tensor and ∇v is the velocity gradient. Both of them are second rank tensors. The double dot indicates a scalar product between them. Thus the entropy generation equation is:

$$T\sigma = -\boldsymbol{\tau}:\nabla v \tag{90}$$

According to the Curie theorem, different tensorial characters cannot couple, and therefore it is helpful to decompose each tensor into its components (isotropic, deviatoric, and anti-symmetric parts):

$$\boldsymbol{\tau} = \tfrac{1}{3}\text{Tr}(\boldsymbol{\tau})\mathbf{I} + \tfrac{1}{2}[\boldsymbol{\tau} + \boldsymbol{\tau}^T - \tfrac{2}{3}\text{Tr}(\boldsymbol{\tau})\mathbf{I}] + \tfrac{1}{2}[\boldsymbol{\tau} - \boldsymbol{\tau}^T] \tag{91}$$

$$\nabla v = \tfrac{1}{3}\text{Tr}(\nabla v)\mathbf{I} + \tfrac{1}{2}[\nabla v + (\nabla v)^T - \tfrac{2}{3}\text{Tr}(\nabla v)\mathbf{I}] + \tfrac{1}{2}[\nabla v - (\nabla v)^T] \tag{92}$$

In the above equations, Tr denotes the trace and $\mathbf{I}$ represents the unit tensor or identity matrix. When a scalar product is formed between the above two tensors for the entropy generation term, only the products between the same tensorial characters survive, that is, between isotropic tensors, between deviatoric tensors, and between anti-symmetric tensors. Therefore, the linear flux equations are as follows:

$$\tfrac{1}{3}\text{Tr}(\boldsymbol{\tau})\mathbf{I} = -L_s/3\text{Tr}(\nabla v)\mathbf{I} = -L_s/3(\nabla \cdot v)\mathbf{I} \tag{93}$$

$$\tfrac{1}{2}[\boldsymbol{\tau} + \boldsymbol{\tau}^T - \tfrac{2}{3}\text{Tr}(\boldsymbol{\tau})\mathbf{I}] = -\tfrac{1}{3}L_d[\nabla v + (\nabla v)^T - \tfrac{1}{3}(\nabla \cdot v)\mathbf{I}] \tag{94}$$

$$\tfrac{1}{2}[\boldsymbol{\tau} - \boldsymbol{\tau}^T] = -\tfrac{1}{3}L_a[\nabla v - (\nabla v)^T] \tag{95}$$

Here L_s, L_d, and L_a are phenomenological coefficients. The following viscosity coefficients are defined:

$\kappa = L_s/3$: bulk viscosity (96)

$\mu = L_d/2$: shear viscosity (97)

$v=L_a/2$: rotational viscosity (98)

When Eqs. (93), (94), and (95) are added up; we can reconstruct the stress tensor as:

$$\tau=(2\mu/3-\kappa)(\nabla\bullet v)\mathbf{I}-\mu[\nabla v+(\nabla v)^T]-v[\nabla v-(\nabla v)^T]$$ (99)

For an irrotational fluid, the anti-symmetric part will drop out. Therefore, the stress tensor for a Newtonian fluid is simplified as:

$$\tau=(2\mu/3-\kappa)(\nabla\bullet v)\mathbf{I}-\mu[\nabla v+(\nabla v)^T]$$ (100)

This equation is known as the constitutive equation for Newtonian fluids in continuum mechanics. It is widely used in the chemical engineering textbooks by Bird et al. [2002], Denn [1980], Fitts [1962], and Whitaker [1968]. Owing to the Curie theorem, all coupling terms have perished; the final equation would otherwise have been quite complicated.

This example clearly illustrates the usefulness of the Curies theorem and the wide applicability of NT.

PROCEDURE OF NONEQUILIBRIUM THERMODYNAMIC STUDY

It would be helpful to summarize how one can approach the NT systematically to study a given transport problem. First, one should get all transport equations for the system, such as equation of continuity, and balance equations for momentum transfer, energy transfer, mass transfer, electrical charge transfer, and entropy transfer. For entropy transfer, the balance equation for entropy (entropy transport) is used, just like any of the other balance equations mentioned above, rather than the entropy generation equation (Eq. (1)).

Second, all necessary governing equations are combined to obtain the net internal entropy generation expression $T\sigma$. This step is well explained by de Groot and Mazur [1962] and Fitts [1962] for many transport systems.

Third, this entropy generation term, which is a scalar product, is split into the appropriate fluxes and forces. At this point, it is unknown if the initial choice of fluxes and forces would guarantee the reciprocal relations. Only the parts of the fluxes with symmetric phenomenological coefficients and the same forces should be used. The mathematical entities of the fluxes and forces may be scalars, vectors, or tensors. The Curie theorem is applied, if appropriate, to simplify the equations.

Fourth, the linear equations that relate the fluxes and forces are written down.

Fifth, the Onsager reciprocal relations are used to study the coupling phenomena.

Sixth, the flux equations are inspected to see whether any new coupling terms may offer new physical phenomena (or predict one).

Seventh, the fluxes and forces are transformed to better describe the system or for more convenient use in interpreting laboratory data.

CONCLUSION

Nonequilibrium thermodynamics can be quite useful in studying many complex engineering problems. Representation by a proper set of fluxes and forces for a given system is not only important

but also very practical in analyzing experimental measurements. This paper demonstrates how a variety of sets of fluxes and forces may be obtained through transformation. The selection of an appropriate set of fluxes and forces can provide a better understanding of irreversible phenomena and a means of analysis for laboratory data. The general formalism may frequently come in an abstract form when the entropy production rate is derived. However, by transformation of variables one can select more practical sets of fluxes and forces. Examples of ideal gas permeation through membrane, pressure-driven membrane processes, and simultaneous heat and mass transfer clearly demonstrate this flexibility.

Traditionally, the Onsager reciprocal relationships are assumed to be valid for linear flux equations and are always subject to experimental validation. The theoretical justification is based on statistical mechanics as first shown by Onsager [1931a, b], which dealt with microscopic reversibility. On a macroscopic level, as we have seen with Eq. (9), the anti-symmetric parts of the phenomenological coefficients produce fluxes that will cause zero entropy generation. Therefore, we can conclude that the symmetric part of the phenomenological coefficient matrix is sufficient for giving a complete description of any irreversible processes, which means that the Onsager reciprocal relationships should be valid for all irreversible processes.

Finally, selection of an appropriate set of fluxes and forces can focus the coupling phenomena as demonstrated in the case of RO, NF, and UF. The study of coupling is the central issue of NT. As many new applications of coupling effects become practical, the importance of understanding the basic principles and inter-relationships increases, and more useful applications of NT for many engineering problems are possible.

NOMENCLATURE

c	: concentration
f	: fugacity
H	: enthalpy
i	: species
$\mathbf{I}$	: identity tensor
$\mathbf{J}$	: generalized flux
J^*	: diffusion flux
$\mathbf{L}$	: phenomenological coefficient matrix
N	: molar mass flux with respect to stationary coordinates
P	: pressure
$\overline{P}$	: partial pressure
q	: heat flux
R	: gas constant
r	: reflection coefficient
S	: entropy
$\mathbf{S}$	: transformation matrix
T	: absolute temperature
$\mathbf{T}$	: transformation matrix
Tr	: trace of a second rank tensor or matrix
$\overline{V}$	: partial molar volume
$\mathbf{v}$	: velocity vector
$\mathbf{X}$	: generalized driving force
x	: mole fraction
y	: mole fraction in gas phase

∇ : nabla (gradient)

Greek Letters

γ : activity coefficient
κ : bulk viscosity
μ : shear viscosity
ν : rotational viscosity
μ_i : chemical potential of i
π : osmotic pressure
σ : rate of entropy generation
τ : stress tensor

Subscripts

a   : anti-symmetric
D   : diffusional
d   : deviatoric
E   : energy
i   : isotropic
i   : species
n   : number of species
P   : pressure driven
s   : symmetric
s   : solute (salt)
T   : isothermal
V   : volumetric
w   : solvent (water)

Superscripts

*   : diffusion
s   : saturated vapour
T   : transposed
$^{-1}$: inverse
′   : transformed quantity
″   : transformed quantity
| : partial molar property

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