Linear-nonequilibrium thermodynamics theory for coupled heat and mass transport

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Abstract

Linear-nonequilibrium thermodynamics (LNET) has been used to express the entropy generation and dissipation functions representing the true forces and flows for heat and mass transport in a multicomponent fluid. These forces and flows are introduced into the phenomenological equations to formulate the coupling phenomenon between heat and mass flows. The degree of the coupling is also discussed. In the literature such coupling has been formulated incompletely and sometimes in a confusing manner. The reason for this is the lack of a proper combination of LNET theory with the phenomenological theory. The LNET theory involves identifying the conjugated flows and forces that are related to each other with the phenomenological coefficients that obey the Onsager relations. In doing so, the theory utilizes the dissipation function or the entropy generation equation derived from the Gibbs relation. This derivation assumes that local thermodynamic equilibrium holds for processes not far away from the equilibrium. With this assumption we have used the phenomenological equations relating the conjugated flows and forces defined by the dissipation function of the irreversible transport and rate process. We have expressed the phenomenological equations with the resistance coefficients that are capable of reflecting the extent of the interactions between heat and mass flows. We call this the dissipation-phenomenological equation (DPE) approach, which leads to correct expression for coupled processes, and for the second law analysis. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Simultaneous heat and mass transport plays a vital role in various physical, chemical and biological processes, hence a vast amount of work on the subject is available in the literature. Coupled heat and mass transfer occurs in separation by absorption, distillation, and extraction [1–4], in evaporation–condensation [5–7], in drying [8,9], in crystallization and melting [10,11], and in natural convection [12]. These processes occur in important industrial applications. Various formulations and methodologies have been suggested for describing combined heat and mass transport problems. In drying, Guerrier et al. [8] investigated the coupling through the saturation pressure of the mixture, which is the function of both the temperature and the solvent volume fraction. Menshutina and Dorokhov [13] simulated drying in a heterogeneous multiphase system based on nonequilibrium thermodynamics theory, and obtained the new general structures of thermodynamic forces. Mikhailov and Ozisik [14] employed the integral transform technique in the development of the general solutions for various coupled heat and mass diffusion problems. In a recent work, Whitaker [15] investigated the coupled-multiphase transport by the method of closure in which various integrals appeared in the volume-averaged equations are solved. Braun and Renz [6] adapted a numerical approach based on the two-dimensional boundary layer equation for the multicomponent diffusion interactions during condensation. Kaiping and

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Nomenclature

a	defined in Eq. (59)
D	diffusion coefficient
D_T	thermal diffusion coefficient
e_t	total specific energy
e_p	specific energy potential
F	mass force
h	specific enthalpy
j	diffusion flow
J	mass flow
J	flow
k	thermal conductivity
l,L,K	phenomenological coefficients
m	mass
M	molar mass
p	pressure
Q^*	heat of transport
r	degree of coupling
s	specific entropy
s_T	Soret coefficient
S	entropy
t	time
T	absolute temperature
u	specific internal energy

v	specific volume, centre-of-mass or barycentric velocity
z	ratio of phenomenological coefficients, Eq. (80)
w_i	mass fraction of component i
X	thermodynamic force

Greek symbols

δ	unit tensor
ϕ	ratio of irreversibility distribution
Φ_S	entropy generation rate
η	ratio of flows
λ	ratio of forces
μ	chemical potential
ρ	density
σ	stress tensor
τ	viscosity part of stress tensor
Ψ	dissipation function

Subscripts

i, j, k	substances
gen	generation
q	heat related
p	potential
T	at constant temperature
s	entropy related
u	internal energy related

Renz [5] studied the thermal diffusion effects in partial filmwise condensation experimentally and numerically.

Investigation of the coupled processes in biological systems has been expanding rapidly with the new concepts such as biothermal engineering and biotransport. For example, laser applications in surgery, therapy and ophthalmology [16], thermal diffusivity of tissues [17], drug delivery [18], and the cryopreservation [19,20] are some of the coupled heat and mass transfer processes in living systems. Cryopreservation is the suspension of thermally driven reaction and transport processes that cause local mass transfer due to the nonuniform pattern of ice formation and the resulting concentration of solute within the living tissue. De Freitas et al. [19] utilized the linear-nonequilibrium thermodynamics (LNET) theory for the transport of water and cryoprotectant in a multicellular tissue. The way molecules are organized, e.g. the protein folding, and biological order [21–24], biological oscillation [25], membrane transport in biological systems [26] can be studied by the nonequilibrium thermodynamics analysis. Structured stationary states of living systems need a constant supply of energy to maintain their states. The energy flow is coupled with other rate processes and the diffusion of matter. Therefore, it is important to express the interaction in the transport and rate processes properly [19,27–32].

LNET deals with the transport and rate processes, which are irreversible in nature. It is based on the local

thermodynamic equilibrium assumption, which is the extension of thermodynamic relations in equilibrium systems to local nonequilibrium subsystems. LNET evaluates the rate of entropy generation resulting from the irreversibilities taking place in the processes. The Gouy–Stodola theorem states that the entropy generation is directly proportional to the loss of available free energy. The dissipated energy per unit time and per unit volume is called the dissipation function, and is the product of the rate of entropy generation and the absolute temperature. The dissipation function defines the conjugate forces and flows of the processes under consideration. These flows are related to the forces in a linear form with the phenomenological coefficients (PCs) through phenomenological equations (PEs). The PCs obey the Onsager reciprocal relations, which states that the coefficient matrix is symmetrical. As a direct consequence of the Onsager relations, the number of unknown coefficients in the PEs are reduced. The PCs are constants and closely related to the transport coefficients of the rate processes and the coupling between them. The theory of the LNET based on the Onsager relations is highly developed by the work of Prigogine [33], Fitts [34], De Groot [35], Katchalsky and Curran [27], Wisniewski et al. [36], Caplan and Essig [29], Eu [37], Kuiken [38], and by many other researchers. Kedem [39] used LNET to represent the coupling between reactions and flows in anisotropic biological systems. Recently,

Curtis and Bird [40] have generalized Fick's law and the Maxwell–Stefan expression to include thermal, pressure, and forced diffusion in a multicomponent fluid with the help of LNET. Miyazaki et al. [41] developed a nonequilibrium thermodynamic model and discussed the proper definition for the internal energy of multicomponent systems. Ramshaw [42] developed a phenomenological theory for multicomponent diffusion, including thermal diffusion, in gas mixtures in which the species may have different temperatures.

The LNET description of heat and mass transfer is compatible with the classical engineering approach based on the hydrodynamic theory of boundary layer, with transport coefficients and driving forces [43]. The theory of LNET is utilized in the second law analysis, and the dissipation is calculated from the entropy generation, or from the exergy balance on the system [44]. The entropy generation approach is especially important in terms of the process optimality as the individual processes contributing to the entropy generation can be identified and evaluated separately. Through the minimization of the entropy generation a thermodynamic optimum can be achieved for an existing design with a specified task [45]. To this end equipartition of the entropy generation or of the thermodynamic forces can also be used as the criterion for process optimum [46,47]. The second law analysis has especially found applications in thermal engineering [45,48–50]. It is also used in separation processes, and in design [2,51–55]. Many of these studies also searched for a link between thermodynamics and economics. Sieniutycz and Shiner [56] reviewed the various aspects of nonequilibrium thermodynamics together with the second law analysis and chemical engineering comprehensively. San et al. [57], and Paulikakos and Johnson [58] used the control volume approach in the second law analysis of combined heat and mass transfer. San et al. [57] used the analogy between heat and mass transfer, and evaluated the degree of coupling by an order of magnitude analysis for a binary mixture of ideal gases. Carrington and Sun [59,60] utilized nonequilibrium thermodynamics in the second law analysis. However, they did not use the PEs to express the flows or the forces, and neglected the coupling between heat and mass transfer. The expressions developed by San et al. [57] and Bejan [61] are based on the equations for the entropy generation per unit volume in a Newtonian Fluid as given by Hirschfelder et al. [62].

Consequently, the methodology of expressing and evaluating the coupling in heat and mass flows differ greatly in the literature. Sun and Carrington [63], and Carrington and Sun [60] noted shortcomings in the second law analysis and in expressing the coupling between heat and mass transfer due to the use of the absolute mass instead of diffusion flow in the control volume method. In the LNET analysis, the transport and rate processes are expressed in the form of the PEs. These equations are capable of displaying the interactions between the various transport and rate processes through the cross-phenomenological coefficients [29]. For the PEs to be useful to this end they must have the conjugate flows and forces defined by the dissipation function resulting from the canonical expressions for open thermodynamic systems. Therefore, in this contribution we use the theory of LNET to express the PEs based on the dissipation function, then define the coupling between the heat and mass transfer. We refer to this as the dissipation-phenomenological equation (DPE) approach. This approach is especially useful if there is no large temperature and concentration differences in a system. Otherwise, it may be advantageous to refer forces and flows to the entropy generation. DPE approach is thermodynamically sound, and can be extended to analyze the coupling for the various irreversible flows and chemical reactions.

2. Local thermodynamic equilibrium

Systems that are not in thermodynamic equilibrium are nonhomogeneous systems in which at least some of the intensive parameters are functions of time and/or position. A local state of a substance is considered as small elementary volumes of the system that is not in thermodynamic equilibrium. These small volumes should contain a sufficient number of molecules for a macroscopic theory to be applicable. When the local thermodynamic equilibrium holds, the specific entropy and specific internal energy in each volume element are evaluated as in a system at equilibrium, and the Gibbs relation and the Gibbs–Duhem relation are applicable. For a nonequilibrium system, the pressure has the same dependence on the specific internal energy u and specific volume v, as in an equilibrium system, i.e., $p = (\partial u / \partial v)_s$. The assumption of local thermodynamic equilibrium holds for great variety of rate processes in physics, chemistry and biological system [29,33–36,56].

3. Phenomenological equations (PEs)

Potential gradients can produce irreversible changes, and are called 'forces', and denoted by X_i ($i = 1, 2, \ldots, n$) for n gradients. The forces produce certain irreversible phenomena such as mass diffusion called the 'flows' (fluxes), and symbolized as J_i ($i = 1, 2, \ldots, n$). Generally any force can cause any flow $J_i(X_i)$ ($i = 1, 2, \ldots, n$). We know, for example that a concentration gradient and a temperature gradient could both produce mass flows as well as heat flows. If the forces vanish, the system goes to an equilibrium state in which the flows

are zero $J_i(X_i = 0) = 0$. The PEs are based on the linear relationships between the flow and force, and any flow is the result of all the forces

$$J_i = \sum_{i=1}^{n} L_{ik} X_k \quad (k = 1, 2, \ldots, n). \tag{1}$$

The coefficients L_{ik} are called the PCs, and defined by

$$L_{ik} = \left(\frac{\partial J_i}{\partial X_k} \right)_{X_j} = \left(\frac{J_i}{X_k} \right)_{X_{j=0}} \quad (j \neq k), \tag{2}$$

where L_{ik} represents flow per unit force and has the characteristics of conductance. The coefficients with the same indices L_{ii}, for example the diffusion coefficient, relate the conjugate force and generalized flow, namely the diffusion and the concentration gradient. The coefficients L_{ik} with $i \neq k$ are known as the cross-coefficients, and related to the coupled transport coefficients, such as the thermal diffusion coefficient. Onsager's fundamental theorem states that, provided a proper choice is made for the flows and forces the matrix of L_{ik} is symmetric

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \ldots, n). \tag{3a}$$

These identities are known as the Onsager reciprocal relations, and can be derived from the principle of microscopic reversibility, using the statistical thermodynamics [64]. Gambar and Markus [65] showed that the Onsager reciprocal relations are the results of the global gauge symmetries of the Lagrangian, which is related to the entropy production of the system considered. This means that the results in general are valid for an arbitrary process. The explicit equations for the Onsager relations depend on the nature of the system, and various kinds of coupling between flows and forces are possible. Classical statistical mechanical theory shows that the Onsager reciprocal relations are valid for diffusion and heat flow for a particular set of flows and forces [34]. All the PCs with the similar and dissimilar indices must satisfy the conditions

$$L_{ii} \geqslant 0 \quad (i = 1, 2, \ldots, n), \tag{3b}$$

$$L_{ii} L_{kk} \geqslant L_{ik}^2 \quad (i \neq k; \quad i, k = 1, 2, \ldots, n). \tag{3c}$$

If there is no metastable equilibrium and all the forces and flows are independent, the inequality sign holds in Eqs. (3b) and (3c).

It is known that the forces are also functions of the flows $X_i(J_k)$ $(k = 1, 2, \ldots, n)$. Using the Maclaurin series expansion and considering the first-order approximation of linear relationships

$$X_i = X_i(J_k = 0) + \sum_{k=1}^{n} \frac{\partial X_i}{\partial J_k} J_k + \cdots \tag{4}$$

we can express the linear PEs in the form

$$X_i = \sum_{i=1}^{n} K_{ik} J_k \quad (k = 1, 2, \ldots, n), \tag{5}$$

where the new PCs are defined as

$$K_{ik} = \left(\frac{\partial X_i}{\partial J_k} \right)_{J_j} = \left(\frac{X_i}{J_k} \right)_{J_{j=0}} = L_{ik}^{-1} \quad (k \neq j), \tag{6a}$$

where L_{ik}^{-1} is the inverse of the matrix L_{ik}. The coefficients K_{ik} have the units of force per unit of flow and represent the generalized resistance. The following relation links the L and K

$$K_{ik} = \frac{|L|_{ik}}{|L|}, \tag{6b}$$

where $|L|$ is the determinant of the L, and $|L|_{ik}$ is the principal minor (see Appendix A). The matrix K also obeys the Onsager relations, and satisfies the conditions [35].

$$K_{ik} = K_{ki}; \quad K_{ii} > 0; \quad K_{ii} K_{kk} \geqslant K_{ik}^2$$
$$(i \neq k; \; i, k = 1, 2, \ldots, n). \tag{6c}$$

The PCs are not functions of the thermodynamic forces and the generalized flows. However, they can be functions of the parameters of the local state T, p and the concentrations w_i as well as the nature of the system [36,37,66].

When we consider a diffusion $\mathbf{j}_i$ which has a tensorial rank of 1, which is a vector, and a concentration gradient X_k also of tensorial rank 1, then the coefficient L_{ik} is a scalar quantity that is consisted with the isotropic character of the system. So that the coefficients L_{ik} do not vanish and the flow $\mathbf{j}_i$ and the force X_k can interact. We observe, therefore the coupling or the cross effects between the various diffusion flows, and between diffusion and heat flows. According to the Curie–Prigogine principal [29], there will be no coupling between scalar and vectorial quantities in an isotropic system. However the scalar quantities, such as chemical reactions, can cause the flow of a substance across an anisotropic membrane producing the active transport in biological systems [27,33].

4. Dissipation function

The time derivative of the entropy is the rate of entropy generation. The LNET evaluates the rate of entropy generation for a specified task of a process. This evaluation (as explained in Section 5) is based on the hypotheses of positive and definite entropy production and of the Gibbs relation

$$T \, ds = du + p \, dv - \sum \mu_i \, dw_i, \tag{7}$$

where u is the specific internal energy, v the specific volume, p the pressure, μ_i the chemical potential and w_i is the mass fraction of substance i. This fundamental relation, valid even away from thermostatic equilibrium, shows that the entropy depends explicitly only on energy, volume and concentrations. If the entropy generation inside the system S_i [33] is taken per unit time t and per unit volume v, it is called the volumetric rate of entropy generation Φ_S, which is a positive and definite quantity

$$\Phi_S = \frac{\mathrm{d}S_i}{\mathrm{d}t\,\mathrm{d}v} \geqslant 0. \tag{8}$$

The dissipation function, Ψ is given by

$$\Psi = T\Phi_S \geqslant 0 \tag{9}$$

and shows that irreversibility causes the decrease in the free energy, in agreement with the Gouy–Stodola theorem [45,67].

The quantities Φ_S and Ψ may be expressed as the sum of the products of the conjugate forces and flows stemming from the second law of thermodynamics [33]

$$\Phi_S = \sum_{i=1}^{n} J_i' X_i' \geqslant 0, \tag{10}$$

$$\Psi = T\Phi_S = \sum_{i=1}^{n} J_i X_i \geqslant 0. \tag{11}$$

Here J_i and J_i' are the generalized flows, and X_i and X_i' are the thermodynamic forces. The quantities Φ_S and Ψ are scalars, and the dot product of two vectors for the case of heat and mass flows. The choice of thermodynamic forces must be made so that in the equilibrium state when the thermodynamic forces vanish ($X_a = 0$), the entropy generation must also vanish. The quantities Φ_S and Ψ depend on the mode of change between given states.

If Eq. (1) is introduced into the dissipation function of Eq. (11), we have

$$\Psi = \sum_{i,k=1}^{n} L_{ik} X_i X_k \geqslant 0. \tag{12}$$

Similarly the entropy generation is expressed by

$$\Phi_S = \sum_{i,k=1}^{n} l_{ik} X_i' X_k' \geqslant 0 \tag{13}$$

and the PCs l and L are associated by

$$l_{ik} = T L_{ik}. \tag{14}$$

Eq. (12) may be written in matrix form showing the symmetry between the flows and the forces expressed in Eqs. (1) and (5)

$$\Psi = \mathbf{X}^{\mathrm{T}} \mathbf{L} \mathbf{X} = \mathbf{J}^{\mathrm{T}} \mathbf{K} \mathbf{J} \geqslant 0, \tag{15}$$

where $\mathbf{X}^{\mathrm{T}}$ and $\mathbf{J}^{\mathrm{T}}$ are the transpose of the respective vectors. Eq. (15) shows that the dissipation function is quadratic in form for all forces and all flows.

The dissipation function or the entropy generation describes the flows and the forces that are linearly dependent on each other through the PCs. The form of the expressions for the dissipation function does not uniquely determine the thermodynamic forces or generalized flows. For an open system, for example, we may define the energy flux in various ways. We may also define the diffusion flows in several alternative ways depending on the choice of reference velocity. Thus we may transform the flows and the forces in various ways. This transformation will not affect the dissipation function if the forces and flows are related by PCs that obey the Onsager relations [36].

5. Balance equations of multicomponent fluids

We consider a single phase of fluid mixture with n substances subject to heat and mass transfer without chemical reactions. Using the assumption of the local thermodynamic equilibrium for such a system, balance equations for the mass, momentum, energy and entropy are necessary in deriving the expressions for the entropy generation or the dissipation function. The notation used by Wisniewski et al. [36] has been adopted in the balance equations.

5.1. The mass balance

The mass flow of component i, $\mathbf{J}_i = \rho_i \mathbf{v}_i$, is a vector showing the flow of a substance relative to a motionless coordinate system. The diffusion flow $\mathbf{j}_i$ relative to the mass average velocity $\mathbf{v}$ is

$$\mathbf{j}_i = \rho_i(\mathbf{v}_i - \mathbf{v}), \tag{16}$$

where the mass average velocity is defined by

$$\mathbf{v} = \frac{1}{\rho} \sum_{i=1}^{n} \rho_i \mathbf{v}_i = \sum_{i=1}^{n} w_i \mathbf{v}_i$$

Here $\mathbf{v}_i$ and ρ_i are the velocity and density of substance i, while w_i is the mass fraction. The sum of diffusion flows of all the substances is zero

$$\sum_{i=1}^{n} \mathbf{j}_i = 0 \tag{17}$$

therefore of n diffusion flows, only $n-1$ are independent. The mass and diffusion flows, $\mathbf{J}_i$ and $\mathbf{j}_i$, of substance i are related by

$$\mathbf{J}_i = \mathbf{j}_i + \rho_i \mathbf{v}. \tag{18}$$

The conservation equation for the substance i is

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0. \tag{19}$$

Using the substantial derivative of the density

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho$$

and taking into account that the conservation equation for the total mass obtained from Eq. (19)

$$\frac{d\rho}{dt} + \rho(\nabla \cdot \mathbf{v}) = 0$$

the mass conservation equation is obtained by replacing the density with the specific volume $v = 1/\rho$

$$\frac{dv}{dt} - v(\nabla \cdot \mathbf{v}) = 0. \tag{20}$$

The balance equation for the amount of substance i can also be written in terms of the mass fraction, w_i

$$\rho \frac{dw_i}{dt} + \nabla \cdot \mathbf{j}_i = 0. \tag{21}$$

5.2. The momentum balance

The Newton's second law of motion states that the change in the momentum of a body is equal to all the forces acting on that body. The forces acting on the volume of fluid can be divided into a mass force $\mathbf{F}$, and a surface force due to the stress tensor σ. If $\mathbf{F}_i$ is the force exerted per unit mass of substance i, then

$$\mathbf{F} = \frac{1}{\rho} \sum_{i=1}^{n} \rho_i \mathbf{F}_i = \sum_{i=1}^{n} w_i \mathbf{F}_i \tag{22}$$

is the force exerted per unit mass of the fluid. Using the pressure force ∇p and the viscous force $\nabla \cdot \tau$ for the surface force, and the body force per unit volume $\rho \mathbf{F}$, the momentum balance equation is given in the substantial form by

$$\rho \frac{d\mathbf{v}}{dt} + \nabla p - \nabla \cdot \tau - \rho \mathbf{F} = 0 \tag{23}$$

The viscosity stress is negligible ($\tau = 0$) in a fluid which is in mechanical equilibrium where the acceleration vanishes ($d\mathbf{v}/dt = 0$). Consequently the pressure gradient is equal to the sum of the mass forces

$$\nabla p - \rho \mathbf{F} = 0. \tag{24}$$

5.3. The energy balance

The local energy balance equation is that the rate of change of the total energy per unit volume is related to a convection flux $\rho e \mathbf{v}$ and a conduction flux $\mathbf{J}_{et}$

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot (\rho e \mathbf{v}) + \nabla \cdot \mathbf{J}_{et} = 0. \tag{25}$$

The total specific energy e of a substance consists of the specific internal energy u, the specific kinetic energy $(1/2)v^2$, and the specific potential energy e_p

$$e = u + \frac{1}{2}v^2 + e_p, \tag{26}$$

where v^2 is the result of $\mathbf{v} \cdot \mathbf{v}$.

The conduction flux $\mathbf{J}_{et}$ of the total energy consists of the conduction flux $\mathbf{J}_u$ of the internal energy, the potential energy flux $\sum_{i=1}^{n} e_{pi} \mathbf{j}_i$ due to diffusion of substances, and the surface work $- \mathbf{v} \cdot \sigma$

$$\mathbf{J}_{et} = \mathbf{J}_u + \sum_{i=1}^{n} e_{pi} \mathbf{j}_i - \mathbf{v} \cdot \sigma. \tag{27}$$

The rate of the change of total kinetic and potential energy per unit volume is [36]

$$\frac{\partial}{\partial t} \rho \left(\frac{1}{2}v^2 + e_p \right)$$
$$= -\nabla \cdot \left[\rho \left(\frac{1}{2}v^2 + e_p \right) \mathbf{v} - \mathbf{v} \cdot \sigma + \sum_{i=1}^{n} e_{pi} \mathbf{j}_i \right]$$
$$- \sigma : (\nabla \mathbf{v}) - \sum_{i=1}^{n} \mathbf{j}_i \cdot \mathbf{F}_i, \tag{28}$$

where $\mathbf{F}_i$ is body force, and is associated with the specific potential energy e_{pi} of substance i by

$$\mathbf{F}_i + \nabla e_{pi} = 0.$$

We subtract Eq. (28) from Eq. (25) to obtain the rate of change of the internal energy per unit volume

$$\rho \frac{du}{dt} + \nabla \cdot \mathbf{J}_u + p(\nabla \cdot \mathbf{v}) - \tau : \nabla \mathbf{v} - \sum_{i=1}^{n} \mathbf{j}_i \cdot \mathbf{F}_i = 0. \tag{29}$$

If diffusion is slow, and the condition of local thermodynamic equilibrium is satisfied, then the rate of change of total energy of all components per unit volume is given by

$$\frac{\partial}{\partial t} \left[\sum_{i=1}^{n} \rho_i \left(\bar{u}_i + \frac{1}{2}v_i^2 + e_{pi} \right) \right]$$
$$= \frac{\partial}{\partial t} \left[\rho \left(u + \frac{1}{2}v^2 + e_p \right) \right], \tag{30}$$

where $\bar{u}_i$ is the partial molar internal energy of substance i.

If $\mathbf{J}_q'$ is the energy flow of pure heat conduction without a flow of internal energy due to diffusion of the substance, the total energy balance, Eq. (25), becomes

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot (\rho e \mathbf{v})$$
$$+ \nabla \cdot \left(\mathbf{J}_q' + \sum_{i=1}^{n} \bar{u}_i \mathbf{j}_i + \sum_{i=1}^{n} e_{pi} \mathbf{j}_i - \mathbf{v} \cdot \sigma \right) = 0. \tag{31}$$

Comparison of this equation with Eq. (27) yields

$$\mathbf{J}_u = \mathbf{J}_q' + \sum_{i=1}^{n} \bar{u}_i \mathbf{j}_i. \tag{32}$$

The second term on the right-hand side of this equation is the net internal energy flow due to the diffusion of substances.

5.4. The entropy balance

The entropy balance equation in terms of the convection entropy flow $\rho s \mathbf{v}$, the conduction entropy flow $\mathbf{J}_S$, and the entropy generation Φ_S is given by

$$\frac{\partial(\rho s)}{\partial t} + \nabla \cdot (\rho s \mathbf{v}) + \nabla \cdot \mathbf{J}_S - \Phi_S = 0. \tag{33}$$

The entropy flux due to conduction is composed of two contributions: one is due to the heat flux in the entropy balance equation $\mathbf{J}_q''$, and the other arising from the diffusion flow $\mathbf{j}_i$

$$\mathbf{J}_S = \frac{\mathbf{J}_q''}{T} + \sum_{i=1}^{n} \bar{s}_i \mathbf{j}_i, \tag{34}$$

where $\bar{s}$ is the partial entropy of substance i. Inserting Eq. (34) into Eq. (33), and using the substantial derivative gives

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot \left(\frac{\mathbf{J}_q''}{T} + \sum_{i=1}^{n} \bar{s}_i \mathbf{j}_i \right) - \Phi_S = 0. \tag{35}$$

Assuming that local thermodynamic equilibrium is valid, we can use the Gibbs relation in terms of specific quantities

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}v - \sum_{i=1}^{n} \mu_i \, \mathrm{d}w_i, \tag{36}$$

where μ_i is the chemical potential of substance i. Differentiation of Eq. (36) with respect to time yields

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\rho}{T} \frac{\mathrm{d}u}{\mathrm{d}t} + \frac{\rho p}{T} \frac{\mathrm{d}v}{\mathrm{d}t} - \frac{\rho}{T} \sum_{i=1}^{n} \mu_i \frac{\mathrm{d}w_i}{\mathrm{d}t}. \tag{37}$$

After substituting Eqs. (29), (20) and (21) into Eq. (37), we have

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{\nabla \cdot \mathbf{J}_u}{T}$$
$$+ \frac{1}{T} \tau : (\nabla \mathbf{v}) + \frac{1}{T} \sum_{i=1}^{n} \mathbf{j}_i \cdot \mathbf{F}_i + \frac{1}{T} \sum_{i=1}^{n} \mu_i (\nabla \cdot \mathbf{j}_i). \tag{38}$$

Using the following transformations

$$\frac{\nabla \cdot \mathbf{J}_u}{T} = \nabla \cdot \left(\frac{\mathbf{J}_u}{T} \right) + \frac{1}{T^2} \mathbf{J}_u \cdot \nabla T$$

and

$$\frac{\mu_i}{T} (\nabla \cdot \mathbf{j}_i) = \nabla \cdot \left(\frac{\mu_i}{T} \mathbf{j}_i \right) - \mathbf{j}_i \cdot \nabla \left(\frac{\mu_i}{T} \right).$$

Eq. (38) becomes

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot \left(\frac{1}{T} \left(\mathbf{J}_u - \sum_{i=1}^{n} \mu_i \mathbf{j}_i \right) \right) + \frac{1}{T^2} \mathbf{J}_u \cdot \nabla T$$
$$+ \frac{1}{T} \sum_{i=1}^{n} \mathbf{j}_i \cdot \left[T\nabla \left(\frac{\mu_i}{T} \right) - \mathbf{F}_i \right] - \frac{1}{T} \tau : (\nabla \mathbf{v}) = 0. \tag{39}$$

Using the relation between the chemical potential and enthalpy given by

$$\mu_i = \bar{h}_i - T\bar{s}_i = \bar{u}_i + p\bar{v}_i - T\bar{s}_i \tag{40}$$

we can find the following relationship between the heat flux $\mathbf{J}_q''$ appearing in the entropy balance equation and the heat flux $\mathbf{J}_q'$ occurring in the energy balance, Eq. (31)

$$\mathbf{J}_q' = \mathbf{J}_q'' + \sum_{i=1}^{n} \bar{h}_i \mathbf{j}_i, \tag{41}$$

where $\bar{h}_i, \bar{v}_i$ are the partial molar enthalpy and velocity, respectively.

The definition of heat flow can be based on a macroscopic energy balance or entropy balance. The internal energy of a substance results from the molecular kinetic energy and the potential energy of the intermolecular interactions. The change of kinetic energy is due to the diffusion for the collision free movement of substances. When the kinetic energy changes as the result of molecular collisions, it is defined as heat conduction. However definition of the potential energy are not uniquely associated with diffusion and conduction due to the complex interactions for each pair of substances. Fitts [34] called the $\mathbf{J}_q''$ as the second law heat flow which is related to the $\mathbf{J}_q'$ by Eq. (41). From Eqs. (35) and (39), the local entropy generation per unit volume is defined by ignoring the viscosity stress, and given by

$$\Phi_S = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^{n} \mathbf{j}_i \cdot \left[T\nabla \left(\frac{\mu_i}{T} \right) - \mathbf{F}_i \right]$$
$$= \Phi_q + \Phi_d. \tag{42}$$

With the following forces defined as:

$$X_q = \nabla \left(\frac{1}{T} \right) \quad \text{(for heat transfer)}, \tag{43}$$

$$X_i = \frac{\mathbf{F}_i}{T} - \nabla \left(\frac{\mu_i}{T} \right) \quad \text{(for mass transfer)}. \tag{44}$$

Eq. (42) expresses the entropy generation as the sum of two distinctive contributions as a result of the product of the flows and the forces: These are the entropy production associated with heat transfer $\Phi_q = \mathbf{J}_u X_q$, and the entropy production due to mass transfer $\Phi_d = \sum_{i=1}^{n} \mathbf{j}_i X_i$.

Entropy generation relation defines the independent forces and the flows to be used in the PEs.

6. Heat and mass transfer coupling

In the DPE approach, we start with the dissipation function $\Psi = T\Phi$, which can be expressed using Eq. (42), as

$$\Psi = -\mathbf{J}_u \cdot \nabla \ln T - \sum_{i=1}^{n} \mathbf{j}_i \cdot \left[T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i \right]. \qquad (45)$$

A transformation is useful for Eq. (45). For that, firstly we use the total potential, which is the summation of the chemical potential and the potential energy $\mu' = \mu + e_p$, and the thermodynamic force for the diffusion becomes

$$T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i = \nabla_T \mu'_i - \frac{\bar{h}_i \nabla T}{T}, \qquad (46)$$

where $\nabla_T \mu'_i$ is the gradient of the total potential at constant temperature, and given by

$$\nabla_T \mu'_i = \nabla \mu_i + \bar{s}_i \nabla T + \nabla e_{pi} = \nabla \mu'_i + \bar{s}_i \nabla T.$$

Secondly, we express the internal energy flux $\mathbf{J}_u$ in terms of $\mathbf{J}''_q$ using Eqs. (32) and (40)

$$\mathbf{J}_u = \mathbf{J}''_q + \sum_{i=1}^{n} \bar{h}_i \mathbf{j}_i. \qquad (47)$$

So that, with the help of Eqs. (46) and (47) and noting that only $n-1$ diffusion flows $\mathbf{j}_i$ are independent, Eq. (17), we have the form for the dissipation function in which all the forces are independent

$$\Psi = -\mathbf{J}''_q \cdot \nabla \ln T - \sum_{i=1}^{n-1} \mathbf{j}_i \cdot \nabla_T (\mu'_i - \mu'_n). \qquad (48)$$

We may now establish the PEs for the vector flows of $\mathbf{J}''_q$ and $\mathbf{j}_i$ and the forces $-\nabla \ln T$ and $-\nabla_T(\mu'_i - \mu'_n)$, and write the linear relations between the flows and the forces

$$-\mathbf{J}''_q = L_{qq} \nabla \ln T + \sum_{j=1}^{n-1} L_{qj} \nabla_T (\mu'_j - \mu'_n), \qquad (49)$$

$$-\mathbf{j}_i = L_{iq} \nabla \ln T + \sum_{j=1}^{n-1} L_{ij} \nabla_T (\mu'_j - \mu'_n)$$

$$(i = 1, 2, \ldots, n-1). \qquad (50)$$

Eqs. (49) and (50) make it possible to define uniquely the PCs that obey the Onsager reciprocal relations

$$L_{qi} = L_{iq}; \quad L_{ij} = L_{ji} \quad (i, j = 1, 2, \ldots, n-1). \qquad (51)$$

The coefficient L_{qq} is associated to the thermal conductivity, while the cross-coefficients L_{iq} and L_{qi} define

the coupling, namely the thermal diffusion (Soret effect) and the heat flow due to the diffusion of substance i (Dufour effect), respectively. These effects are generally referred to the forces, namely to the gradients of temperature and composition. To this end we should take into account the fact that the roles of forces and flows are symmetric. For multicomponent diffusion, the matrix L includes L_{ii} and L_{ij}. The coefficients L_{ii} are associated to the diffusion flow $\mathbf{j}_i$ arising from its own chemical potential gradient of substance i, while the coefficients L_{ij} define the part of $\mathbf{j}_i$ arising from the chemical potential gradients of substance j. The coefficients L_{ij} result from the intermolecular interactions of the dissimilar molecules. If the coefficients L_{ij} are negative, diffusion of j causes a diffusion flow of i in the opposite direction. In principle, each PC is uniquely determined, and may be measured by a suitable experiment [34].

The thermal diffusivity may be related to a new quantity called the heat of transport. To understand the concept consider expressing the thermodynamic force, using the resistance type coefficients K_{ij}, from Eq. (50)

$$\nabla_T (\mu'_j - \mu'_n) = -\sum_{i=1}^{n-1} K_{ji} (\mathbf{j}_i + L_{iq} \nabla \ln T)$$

$$(j = 1, 2, \ldots, n-1), \qquad (52)$$

where $K_{ji} = L_{ij}^{-1}$.

This thermodynamic force can be inserted into Eq. (49), and we have

$$-\mathbf{J}''_q = \left(L_{qq} - \sum_{i,j=1}^{n-1} L_{iq} L_{qj} K_{ji} \right) \nabla \ln T - \sum_{i,j=1}^{n-1} L_{qj} K_{ji} \mathbf{j}_i. \qquad (53)$$

The heat of transport, Q_i^* of component i is expressed by

$$Q_i^* = \sum_{j=1}^{n-1} L_{qj} K_{ji} = \sum_{j=1}^{n-1} L_{qj} L_{ij}^{-1} \quad (i = 1, 2, \ldots, n-1) \qquad (54)$$

and can be used in the PEs to eliminate the coefficients L_{qj} or L_{jq}. For example after introducing the heat of transport, Eq. (53) becomes

$$-\mathbf{J}''_q = \left(L_{qq} - \sum_{i,j=1}^{n-1} L_{iq} Q_i^* \right) \nabla \ln T - \sum_{i,j=1}^{n-1} Q_i^* \mathbf{j}_i. \qquad (55)$$

In an isothermal system where $\nabla \ln T = 0$, Eq. (55) yields

$$\mathbf{J}''_q = \sum_{i=1}^{n-1} Q_i^* \mathbf{j}_i \quad \text{and} \quad Q_i^* = \left(\frac{\mathbf{J}''_q}{\mathbf{j}_i} \right)_T. \qquad (56)$$

Eq. (56) indicates that the heat of transport Q_i^* is the heat flow to keep temperature constant when diffusion flow of substance i takes place. The heat of transport in Eq. (56) is based on $\mathbf{J}''_q$, and on the diffusion flow referred to the mass average velocity. So that the definition

of it varies with the choice of the heat flow and the diffusion flow. We may use the Onsager reciprocal relations to relate the heat of transport to the thermal diffusion coefficients, and it is then possible to obtain experimental values of heats of transport.

For a multicomponent fluid at mechanical equilibrium (see Eq. (24)), the Gibbs–Duhem relation at constant temperature yields

$$\sum_{i=1}^{n} w_i \nabla_T \mu_i' = 0, \tag{57}$$

where the gradient of total potential in the absence of mass forces ($\mathbf{F}_i = 0$) is given by

$$\nabla_T \mu_i' = \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial w_k} \right)_{T,p,w_{i \neq k}} \nabla w_k. \tag{58}$$

Eq. (57) enables us to eliminate $\nabla_T \mu_n'$ from Eq. (48), and we have

$$\Psi = -\mathbf{J}_q'' \nabla \ln T - \sum_{i,k=1}^{n-1} \mathbf{j}_i \cdot a_{ik} \left[\sum_{j=1}^{n-1} \left(\frac{\partial \mu_k}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j \right], \tag{59}$$

where $a_{ik} = \delta_{ik} + w_k/w_n$, and δ_{ik} is the unit tensor. We can now establish the following new set of PEs based on the dissipation function of Eq. (59)

$$-\mathbf{J}_q'' = L_{qq} \nabla \ln T + \sum_{i,k,j=1}^{n-1} L_{qj} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j, \tag{60}$$

$$-\mathbf{j}_i = L_{iq} \nabla \ln T + \sum_{i,k,j=1}^{n-1} L_{ij} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j$$
$$(i = 1, 2, \ldots, n-1) \tag{61}$$

Based on the rate of entropy generation form of Eqs. (48) and (14) the PEs of Eqs. (60) and (61) can also be expressed as

$$-\mathbf{J}_q'' = l_{qq} \nabla \left(\frac{1}{T} \right) + \sum_{i,k,j=1}^{n-1} l_{qj} \frac{1}{T} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j, \tag{62}$$

$$-\mathbf{j}_i = l_{iq} \nabla \left(\frac{1}{T} \right) + \sum_{i,k,j=1}^{n-1} l_{ij} \frac{1}{T} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j. \tag{63}$$

Furthermore, Eqs. (60) and (61) can be transformed to a new set of PEs by replacing the coefficients L with the coefficients K, given by Eq. (6a). Since the K is the inverse matrix of L, the coefficients of K reflect the direct interference when several flows interact in the system. We now therefore consider the symmetry between the flows and forces, and Eqs. (60) and (61) become

$$-\nabla \ln T = K_{qq} \mathbf{J}_q'' + \sum_{j=1}^{n-1} K_{qj} \mathbf{j}_i \quad (i = 1, 2, \ldots, n-1), \tag{64}$$

$$-\nabla w_j = K_{iq} \mathbf{J}_q'' + \sum_{j=1}^{n-1} K_{ij} \mathbf{j}_i \quad (i = 1, 2, \ldots, n-1). \tag{65}$$

In Eqs. (64) and (65), we express the thermodynamic forces as a function of conjugate flows which are easy to control experimentally. Kedem [39] also used a similar form of the PEs to express active transport, that is the coupled processes of flows and chemical reactions in biological systems with anisotropic character.

When the temperature gradient vanishes, ($\nabla T = 0$), the diffusion flow is given by

$$\mathbf{j}_i = -\rho \sum_{j=1}^{n-1} D_{ij} \nabla w_j \quad (i = 1, 2, \ldots, n-1). \tag{66}$$

Comparing Eqs. (61) and (66) yields the diffusion coefficient, defined by

$$D_{ij} = \frac{1}{\rho} \sum_{k,j=1}^{n-1} L_{ij} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right) \quad (i = 1, 2, \ldots, n-1). \tag{67}$$

When the concentration gradient vanishes, $\nabla w_i = 0$, we have the thermal diffusion, in which mass flows are due to the gradient of temperature, and Eq. (61) gives

$$\mathbf{j}_i = -L_{iq} \nabla \ln T = -\frac{\rho}{T} D_{Ti} \nabla T, \tag{68}$$

where the thermal diffusion coefficient is defined by

$$D_{Tiq} = \frac{L_{iq}}{\rho}. \tag{69}$$

The thermal diffusion ratio k_{Tiq} relates these transport coefficients D_{ij} and D_{Tiq}

$$k_{Tiq} = \frac{D_{Tiq}}{\sum_{j=1}^{n-1} D_{ij}}. \tag{70}$$

Due to the nonideality of the system, the gradient of chemical potential in Eq. (67) and hence k_{Tiq} may become negative. This causes the flow of a substance to a hotter part in the system. Thermal diffusion is usually characterized by the Soret coefficient S_{Tiq}, which is defined as the ratio of the thermal-diffusion coefficient to the ordinary diffusion coefficient

$$S_{Tiq} = \frac{D_{Tiq}}{D_{ij}}. \tag{71}$$

The Soret coefficient is a measure of the concentration gradient of the solute that can be maintained as a result of a temperature gradient at a stationary state, where $\mathbf{j}_i = 0$ and $\nabla T = $ constant. The Soret coefficient is also associated with the heat of transport Q_i^* as follows:

$$s_{Tiq} = Q_i^* \frac{1}{\sum_{j,k=1}^{n-1} a_{ik} \left(\frac{\partial \mu_j}{\partial w_j} \right)_{T,p,w_{i \neq j}}}. \qquad (72)$$

The thermal diffusion factor α is given by $\alpha = T s_{Tiq}$.

From Eq. (60) we can express the Dufour effect, which is the flow of heat caused by only a concentration gradient ($\nabla \ln T = 0$)

$$\mathbf{J}_q'' = - \sum_{i,k,j=1}^{n} L_{qi} a_{ki} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{k \neq j}}. \qquad (73)$$

When we compare Eq. (73) with the combined Eqs. (66) and (67), we can easily see that the Dufour coefficient is defined as $D_{Ci} = L_{qi}/\rho$, and due to the Onsager relations, is equal to thermal diffusion coefficient D_{Tiq}.

In a single component system, the thermomolecular pressure difference is the result of the coupling between heat and mass flows. It is well known as the Knudsen effect in a gas, and fountain effect in a liquid system. When we have a membrane between gases or liquids, the coupling occurs as the thermo-osmosis effect [27,33,64].

It is now straightforward to express the entropy generation or the dissipation function. By substituting Eqs. (62) and (63) into Eq. (13), we can calculate the rate of entropy generation

$$\begin{aligned} \Phi_S &= l_{qq} \left[\nabla \left(\frac{1}{T} \right) \right]^2 \\ &+ \sum_{i,k,j=1}^{n-1} l_{qj} \left[\frac{1}{T} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j \right]^2 \\ &+ 2 \sum_{i,k=1}^{n-1} l_{iq} \nabla \left(\frac{1}{T} \right) \sum_{i,k,j=1}^{n-1} \left[\frac{1}{T} a_{ik} \left(\frac{\partial \mu_i}{\partial w_j} \right)_{T,p,w_{i \neq j}} \nabla w_j \right] \\ &\times (i \neq k), \qquad (74) \end{aligned}$$

where $l_{qj} = l_{iq}$, and the coefficients of l are related to L by Eq. (14). The individual contributions related to heat and mass flows as well as the coupling between them are represented by the first, second and third terms, respectively on the right-hand side of Eq. (74). This equation is the basis of the second law analysis, and useful in many ways. For example we can evaluate the individual contributions in the entropy generation, hence determine the trade off between them. To this end the ratio of the irreversibility distribution ϕ in the volume of a system can be obtained by

$$\phi = \frac{l_{qq} [\nabla(1/T)]^2}{\Phi_S}. \qquad (75)$$

When ϕ approaches to unity, the irreversibility due to heat transfer becomes the dominating part in the entropy generation [45,68]. The nature of the distribution of the entropy generation is also helpful in evaluating the optimality of a system with a required task [46,47].

The most widely adopted applications of Eq. (74) involve the entropy generation minimization with respect to certain parameters in searching a thermodynamically optimum operating conditions and/or a design for a process [56,57,61,67,69]. Before we do that we must evaluate the total entropy generation $\dot{S}_{\text{gen}}$ inside the volume of a given system by

$$\dot{S}_{\text{gen}} = \int_V \Phi_S \, dV = \int_V \left(\sum_{i=1}^{n} j_i X_i \right) dV. \qquad (76)$$

Prigogine [33] showed that for a certain value of the force for the heat flow, the rate of entropy generation becomes minimum at the stationary state where $\mathbf{j}_i = 0$.

We can also use Eqs. (64) and (65) in Eq. (15) to express the dissipation function for coupled heat and mass flows

$$\Psi = K_{qq} \mathbf{J}_q''^2 + \sum_{j=1}^{n-1} K_{ij} \mathbf{j}_i^2 - 2 \sum_{j=1}^{n-1} K_{iq} \mathbf{J}_q'' \cdot \mathbf{j}_i. \qquad (77)$$

Here the first and the second terms on the right-hand side of Eq. (77) are the dissipations due to the heat and mass flows, respectively, while the third term denotes the dissipation due to the coupling.

The degree of the coupling results from the relationships between the forces and the flows. From Eqs. (64) and (65), we can define the ratio of forces ($\lambda = \nabla \ln T / \nabla w_i$) and the flows ($\eta = \mathbf{J}_q''/\mathbf{j}_i$) for a binary mixture. Dividing Eqs. (64) with (65), and further dividing both the numerator and denominator by $(K_{qq}K_{ij})^{1/2} \mathbf{j}_i$, we obtain

$$\lambda = \frac{(K_{qq}/K_{ij})^{1/2} \eta + K_{iq}/(K_{qq}K_{ij})^{1/2}}{K_{iq}/(K_{qq}K_{ij})^{1/2} \eta + (K_{ij}/K_{qq})^{1/2}} \qquad (K_{iq} = K_{qi}). \qquad (78)$$

Eq. (78) shows that the ratio of forces λ varies with the ratio of flows, η. As the quantity $K_{iq}/(K_{qq}K_{ij})^{1/2}$ approaches zero, each flow becomes independent, and we have the ratio of forces approaching $\lambda_i \to (K_{qq}/K_{ij})\eta$. If $K_{iq}/(K_{qq}K_{ij})^{1/2}$ approaches ± 1, then the two forces are not associated with the flows, and the ratio of forces approaches a fixed value $\lambda \to \pm (K_{qq}/K_{ij})^{1/2}$. This case is the situation where the matrix of the PCs becomes singular, and corresponds to the equality sign in Eqs. (3c) and (6c). The ratio

$$r = \frac{-K_{1q}}{(K_{qq}K_{ij})^{1/2}} \qquad (79)$$

indicates the degree of coupling, and it can be used as a base for comparison of systems with several coupled forces. As the heat and mass flows are both the vectors, the sign of r indicates the direction of forces of the substances. If $K_{iq} < 0$ hence $r > 0$, and the flow of a substance may drag another substance in the same di-

rection, however it will flow in the opposite direction if $K_{iq} > 0$ and $r < 0$. For heat and mass flows the dissipation function defines the two limiting values of r between $+1$ and -1 [29]. An incomplete coupling takes a value between these two limits. The coupling may be further clarified by the ratio

$$z^2 = \frac{K_{qq}}{K_{ij}} \tag{80}$$

and Eq. (78) becomes

$$\lambda = \frac{z\eta - r}{1/z - r\eta}. \tag{81}$$

Eq. (81) indicates that for the known values of z and η, the ratio of forces is determined by the degree of coupling r. With complete coupling, λ is equal to z and r becomes $+1$ or -1. The minus sign of η terms from the situations where the differentiation of chemical potential with respect to concentration may have negative values due to nonideality of the mixture. This complex behavior results from solution nonideality of the mixture.

With the help of the z, we can define the reduced force ratio of $z\lambda$, and the reduced flow ratio η/z, and can relate them by

$$z\lambda = \frac{r + \eta/z}{r\eta/z + 1}. \tag{82}$$

Change of the reduced flow ratio with the reduced force ratio in the range $-1 < r < +1$ is given in Fig. 1. After Caplan and Essig [29] two reference stationary states in the coupled processes can be defined as the level flow where $X_i = 0$, and static head where $J_i = 0$. Example of systems at static head are an open circuit fuel cell and active transport in a cell membrane, whereas the examples of systems at level flow are a short circuited fuel cell and salt and water transport in kidneys. In a incompletely coupled systems, a constant supply of energy is necessary to maintain these reference states without output or work.
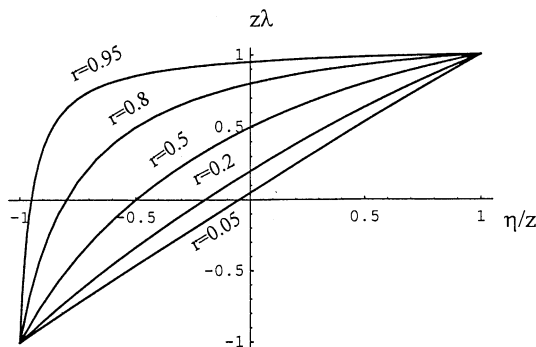

Fig. 1. Change of reduced flows $z\lambda$ with the reduced forces η/z.

7. Conclusions

The coupling between the flows of heat and mass is very important in many industrial processes as well as in the living systems, and it should be accounted for in a proper way. We have demonstrated that the theory of LNET can play crucial role in the proper definition of the coupled heat and mass flows. To this end we have suggested the use of the resistance type of PCs in the PEs, in which the conjugate forces and flows are identified by the dissipation function. We called this procedure as the DPE approach. The dissipation function is the direct result of rigorous and sound theory of LNET based on the assumption of the local thermodynamic equilibrium. We also have demonstrated the vital role played by the PEs in the second law analysis. Since the entropy production depends on the flows and forces, the analysis of LNET defines the correct forces and flows involved in an irreversible process. The role of the PEs is the determination of the true transport coefficients, and the interactions between the flows and forces. This role has been formulated in this study.

Appendix A

We can express the phenomenological equations for two flows and two forces by

$$\mathbf{J}_1 = L_{11}X_1 + L_{12}X_2, \tag{A.1}$$

$$\mathbf{J}_2 = L_{21}X_1 + L_{22}X_2. \tag{A.2}$$

Solving these equations for the thermodynamic forces yields

$$X_1 = K_{11}\mathbf{J}_1 + K_{12}\mathbf{J}_2, \tag{A.3}$$

$$X_2 = K_{21}\mathbf{J}_1 + K_{22}\mathbf{J}_2, \tag{A.4}$$

where

$$K_{11} = \frac{L_{22}}{|L|}; \quad K_{12} = -\frac{L_{12}}{|L|}; \quad K_{21} = -\frac{L_{21}}{|L|}; \quad K_{22} = \frac{L_{22}}{|L|}$$

and

$$|L| = L_{11}L_{22} - L_{12}L_{21}.$$

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