

REVIEW ARTICLES

Nonequilibrium Thermodynamics in Engineering and Science

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The field of nonequilibrium thermodynamics has been a popular one outside the United States, especially in Europe, and scientists there from various disciplines have published extensively on the use of nonequilibrium thermodynamics in a large variety of biological, chemical, and mechanical engineering applications. In contrast, the number of publications from North America has been relatively modest. Here, we review the field of nonequilibrium thermodynamics to assess its utility and impact in engineering and science. We find that developments in the fields thermodynamic optimality of processes, dissipative structures, coupled transport and rate processes, and biological systems suggest that in some circumstances nonequilibrium thermodynamics can be quite useful.

Introduction

The application of thermodynamics to nonequilibrium processes takes many forms. The simplest is based on the assumption of local equilibrium. There it is assumed that even though the system in which a process is occurring is not at global equilibrium, in any small region the thermodynamic properties are related to the state variables in the same manner as in equilibrium. For this assumption to be valid, the internal relaxation processes in the fluid or material must be much faster than the rate of change imposed upon the state variables. The local equilibrium concept is valid for a wide range of macroscopic systems^{1–7} of usual gases and liquids and for most transport processes and chemical reactions where the reactive collision rates are relatively smaller than overall collision rates.⁶ It is not valid in highly rarefied gases where collisions are too infrequent. The extension of equilibrium thermodynamics to nonequilibrium systems with the local equilibrium assumption is a well-accepted form of nonequilibrium thermodynamics (NET).^{1–8} Such an extension is possible in terms of entropy density, $s[T(x), N_k(x)]$, which is a function of the temperature and the mole number densities at location x , when a well-defined local temperature $T(x)$ exists. Consequently, the total entropy and energy can be obtained from the integrals over the volume of the system: $S = \int_V s[T(x), N_k(x)] dV$, and $U = \int_V u[T(x), N_k(x)] dV$.⁶ From the internal energy density $u(x)$, we obtain the local variables of $(\partial s / \partial u)_{N_k} = 1/T(x)$ and $(\partial s / \partial N_k)_u = -\mu(x)/T(x)$.

Another well-known application of thermodynamics to nonequilibrium processes is the so-called second law analysis, or availability or exergy analysis, of real processes. Such an

analysis is based on the Gouy–Stodola theorem, which states that the lost available energy is directly proportional to the entropy production due to irreversibility in a process. This provides a quantitative measure of irreversibility through the level of entropy production, which by the second law of thermodynamics is always positive. The level of entropy production can be used as one criterion of the optimality of a process, mainly related to reducing the irreversibilities to control the dissipation of useful power and the depletion of natural resources.⁹ However, as an availability or exergy analysis does not involve a financial analysis or consideration of materials of construction or other constraints, the process that has the highest second law efficiency may not be the most economical. Indeed, if the highest second law efficiency was all that needed to be considered, all motive power would be supplied by Carnot engines. Nonetheless, a second law analysis can be useful in efficient energy utilization and engineering design,^{10–11} and consequently simulation packages such as recent versions of ASPEN PLUS provide methods of estimating second law efficiency and an exergy analysis for engineering process integration and optimization of, for example, distillation columns, heat exchangers, and chemical reactors.

The next type of nonequilibrium thermodynamic description, and the one that is of more interest to us here, is based on the observation that the level of irreversibility of any step in a process is, as we shall discuss, related to its distance from global equilibrium; this distance may be treated as a parameter of the process.⁶ Small values of this parameter result in processes in which there are linear relations between the driving forces or gradients in the system and the fluxes that result; examples are Fourier's law in heat conduction and Fick's law in diffusion. Unfortunately, this is sometimes interpreted as that NET is a completely linearized theory and applies only to systems close

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to global equilibrium. On the contrary, the NET theory with linear force–flux equations may lead to partial differential equations nonlinear for the thermodynamic state variables.^{4,6} This matter will be elaborated further in the next section. Processes occurring far from global equilibrium lead to nonlinear force–flux relations and in some cases to the spontaneous formation of self-organized dissipative structures such as Bénard cells, tornadoes, oscillatory reactions, and even living cells.^{6,12–15} Such highly organized states are not necessarily far from local equilibrium and can only be maintained by constant external mass and energy fluxes. In 1944, Schrödinger¹⁶ suggested that life is a far-from equilibrium system that maintains its organized state by producing entropy using an external supply of energy and matter, and the study of living systems would reconcile biological organization and classical nonequilibrium thermodynamics.

Since the publication of the Onsager reciprocal relations^{17,18} in 1931, many researchers have been exploring the impact and use of nonequilibrium thermodynamics. Early books in this area were by Prigogine¹ in 1947, Denbigh² in 1951, De Groot³ in 1952, DeGroot and Mazur⁴ in 1962 and 1984, and Fitts⁵ in 1962. A criticism of nonequilibrium or irreversible thermodynamics (IT) is that “...IT has no useful theory, and brings no useful outcome neither for an engineer nor for a scientist; has nothing useful to say about irreversibility in general.” In 1966, Wei¹⁹ stated that “...he had followed irreversible thermodynamics for more than 10 years prior...”, asked “if irreversible thermodynamics produced anything other than journal paper”, and noted that “the applications of irreversible thermodynamics to previously unsolved problems are few and there is no prospect for an immediate increase.” This publication may have adversely affected the scientific community in North America, resulting in a comparatively modest number of U. S. publications in the field of NET. However, NET has been popular in the rest of the world, particularly in Europe. Also, two years after Wei’s paper, Onsager received the Noble Prize in chemistry in 1968 as a result of his reciprocal relations, and in 1977, Prigogine was awarded the Nobel Prize in chemistry, largely for his theory of dissipative structures. The Nobel committee noted that “Prigogine has fundamentally transformed and revised the science of irreversible thermodynamics.”

We feel there is a need to assess the utility of NET in science and engineering. For this purpose, here we revisit the use of the thermodynamics of irreversible processes in engineering by presenting a brief review of the theory of NET and examples of its use.

Theory of Nonequilibrium Thermodynamics

The thermodynamics of irreversible processes uses transport expressions that include, for example, thermal, pressure, and diffusion.²⁰ The NET approach has been widely used to estimate the rate of entropy production in physical, chemical, and biological processes that include heat and fluid flux, heat and mass transport, separations, chemical reactions, and reacting fluxes. In a nonequilibrium system with local equilibrium established, the intensive variables are well-defined locally, while the densities of extensive variables, such as energy and entropy, are defined in terms of local temperature and concentrations. Therefore the thermodynamic variables are functions of position and time.

Change of total entropy of a system is

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad (1)$$

where the first term on the right is the entropy exchange through

the boundary that can be positive, zero, or negative, and the second term is the rate of entropy production, which is always positive. In NET, one estimates the rate of entropy production $\Phi = (d_i S/dt) = \sum_k J_k X_k \geq 0$ or the rate of local dissipation of Gibbs free energy (dissipation function^{22,35}) $\Psi = T\Phi \geq 0$ in terms of a product of a flux J_k (flux) and a force X_k on the system in an irreversible process k . (Ψ is different from the exergy destruction in an irreversible process calculated as the product of entropy production with the dead state, that is, environment, temperature.) However, since a product is involved, it is evident that there is not a unique way of choosing forces and fluxes. For example, a force can be multiplied by a constant and the flux divided by the same constant, and the same dissipation would be obtained. We shall come back to this shortly.

The second law analysis has been extensively utilized in the field of heat and fluid flux. Bejan⁹ presented the basic approach, methodology, and applications of the second law analysis in the thermal engineering field. The local rate of entropy production per unit volume Φ in two-dimensional convective heat transfer is given in Cartesian coordinates by

$$\begin{aligned} \Phi \, dx \, dy = & \frac{q_x + \frac{\partial q_x}{\partial x} dx}{T + \frac{\partial T}{\partial x} dx} dy + \frac{q_y + \frac{\partial q_y}{\partial y} dy}{T + \frac{\partial T}{\partial y} dy} dx - \frac{q_x}{T} dy - \\ & \frac{q_y}{T} dx + \left(s + \frac{\partial s}{\partial x} dx \right) \left(v_x + \frac{\partial v_x}{\partial x} dx \right) \left(\rho + \frac{\partial \rho}{\partial x} dx \right) dy + \\ & \left(s + \frac{\partial s}{\partial y} dy \right) \left(v_y + \frac{\partial v_y}{\partial y} dy \right) \left(\rho + \frac{\partial \rho}{\partial y} dy \right) dx - s v_x \rho \, dy - \\ & s v_y \rho \, dx + \frac{\partial(\rho s)}{\partial t} dx \, dy \quad (2) \end{aligned}$$

The first four terms on the right of eq 2 account for the entropy flux due to heat transfer, the next four terms represent the entropy convected in to and out of the system, and the last term is the rate of entropy accumulation in the control volume. When eq 2 is divided by $dx \, dy$, the local rate of entropy production becomes

$$\begin{aligned} \Phi = & \frac{1}{T} \left(\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} \right) - \frac{1}{T^2} \left(q_x \frac{\partial T}{\partial x} + q_y \frac{\partial T}{\partial y} \right) + \rho \left(\frac{\partial s}{\partial t} + v_x \frac{\partial s}{\partial x} + \right. \\ & \left. v_y \frac{\partial s}{\partial y} \right) + s \left[\frac{\partial \rho}{\partial t} + v_x \frac{\partial \rho}{\partial x} + v_y \frac{\partial \rho}{\partial y} + \rho \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) \right] \quad (3) \end{aligned}$$

The last term on the right of eq 3 vanishes based on the mass conservation principle $d\rho/dt + \rho \nabla \cdot \mathbf{v} = 0$ where d/dt is the substantial derivative. Therefore in vectorial notation the volumetric rate of entropy production is

$$\Phi = \frac{1}{T} \nabla \cdot \mathbf{q} - \frac{1}{T^2} \mathbf{q} \cdot \nabla T + \rho \frac{ds}{dt} \quad (4)$$

By combining the relation $\rho(ds/dt) = (\rho/T)(du/dt) - (P/(\rho T))(-d\rho/dt)$ and the first law of thermodynamics $\rho(du/dt) = -\nabla \cdot \mathbf{q} - P(\nabla \cdot \mathbf{v}) + \tau : \nabla \mathbf{v}$ with eq 4, we obtain the following expression for the entropy production for an incompressible flux:

$$\Phi = -\frac{1}{T^2} (\mathbf{q} \cdot \nabla T) + \frac{1}{T} (\tau : \nabla \mathbf{v}) \quad (5)$$

The term $\tau : (\nabla \mathbf{v})$ represents the conversion of mechanical energy into thermal energy and is the viscous dissipation heating that occurs in all flux systems. This term can be large in fluxes with

high viscosity or large velocity gradients or both, as in high-speed flight, in rapid extrusion, and in lubrication. The viscous dissipation in Newtonian fluids is a sum of squared terms of the velocity gradients and the viscosity in the following form:

$$\tau : \nabla \mathbf{v} = \frac{1}{2} \mu \sum_i \sum_j \left[\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \right]^2 = \mu \Theta \quad (6)$$

where μ is the viscosity and Θ is the viscous dissipation and is always positive. With the use of Fourier's law, $\mathbf{q} = -k \nabla T$, and eq 6, the entropy production becomes

$$\Phi = \frac{k}{T^2} (\nabla T)^2 + \frac{\mu}{T} \Theta \quad (7)$$

For a two-dimensional Cartesian coordinate system, eq 7 can be expressed by

$$\Phi = \frac{k}{T^2} \left[\left(\frac{\partial T}{\partial x} \right)^2 + \left(\frac{\partial T}{\partial y} \right)^2 \right] + \frac{\mu}{T} \left\{ 2 \left(\frac{\partial v_x}{\partial x} \right)^2 + 2 \left(\frac{\partial v_y}{\partial y} \right)^2 + \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right)^2 \right\} \quad (8)$$

The first set of terms on the right of eq 8 is the entropy production due to the heat transfer, $\Phi_{\Delta T}$, and the entropy production due to the fluid friction, $\Phi_{\Delta P}$, is the second set of terms, so the rate of entropy production has the form $\Phi = \Phi_{\Delta T} + \Phi_{\Delta P}$. From this form, an irreversibility distribution ratio may be defined as $Be = \Phi_{\Delta T} / \Phi$ that is called the Bejan number, Be . The irreversibility due to the heat transfer dominates when $Be > 1/2$, while $Be < 1/2$ is the case where the irreversibility due to the friction dominates. The rate of entropy production for convective heat transfer in ducts and the trade offs between the irreversibilities due to heat transfer and friction have been investigated extensively.⁹ One outcome of this is that the inlet temperature difference between the fluid and the wall is an important design criterion to be optimized. More importantly the map of volumetric entropy production rate and the distribution of irreversibility ratio at various thermal boundary conditions can be used to analyze the system. This leads to identifying the level of thermodynamic imperfection under current operating conditions for a fixed design. The next step is then to either seek a better compatibility between operating conditions and design parameters or modify the existing design for a specified operational constraint, such as heat load or production capacity. Optimizing the configuration such as geometry and architecture of nonequilibrium flux is a new and growing trend called the constructal theory.²¹ The NET theory cannot formulate the ways to minimize the entropy production; in general, this requires a concerted effort by engineers and scientist from various disciplines.⁸⁻¹⁰

The conventional theory of nonequilibrium thermodynamics generally uses the following procedure: (1) start with the Gibbs relation in terms of the relevant thermodynamic variables, (2) establish the conservation laws for these variables, (3) establish an entropy balance equation and derive the entropy production or a dissipation function as a sum of products of dissipative fluxes and thermodynamic forces, and (4) use these fluxes and forces in linear phenomenological equations.

By incorporating the entropy balance into the general balance equations of mass, momentum, and energy, nonequilibrium thermodynamic theory can be used to estimate the total dissipation stemming from transport phenomena, chemical reactions, and other effects in a system. The volumetric rate of

TABLE 1: Conjugate Fluxes and Forces Identified by the Dissipation Function (DPE Approach²⁴)^a

process	flux	force
heat flux	$\mathbf{J}_u = L_q X_q$	$X_q = T \nabla(1/T)$
mass flux	$\mathbf{J}_i = L_i X_i$	$X_i = F_i - T \nabla(\mu_i/T)$
viscous effect	$\mathbf{J}_v = L_v X_v$	$X_v = (\nabla v)$
reaction velocity	$J_r = L_r X_r$	$X_r = A_r = -\sum_{i=1}^k \mu_i \nu_{ij}$

^a Where $\nabla(\mu_i/T) = \nabla(\mu_i/T)_T + h_i \nabla(1/T)$.

entropy production $\Phi = d_i S / (dt dV)$ yields the rate of lost work $W_{\text{lost}} = T_o \Phi$ (T_o is the temperature of the environment) or the dissipated energy Ψ , or the loss of Gibbs' free energy $-dG$ for isothermal systems. Since the total volumetric entropy production is directly related to the lost available energy in a system with irreversible processes, it is related to the thermodynamically optimum design of a process.

For a multicomponent fluid system with n components, such a procedure yields the following dissipation function in terms of the conjugate forces X_i and fluxes J_i for l chemical reactions (but excluding the electrical and magnetic effects)²²

$$\Psi = T \Phi = \sum_i J_i X_i = T \left\{ \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_i \cdot \left[T \nabla \left(\frac{\mu_i}{T} \right) - \mathbf{F}_i \right] + \frac{1}{T} \tau : (\nabla v) - \frac{1}{T} \sum_{j=1}^l A_j J_{r,j} \right\} \geq 0 \quad (9)$$

where \mathbf{F}_i is the force per unit mass of component i . In this equation, the rate entropy production is the sum of four separate contributions due to heat transfer, mass transfer, momentum transfer, and chemical reactions. Conjugated forces and generalized fluxes have the same rank of tensor and the same index. A set of the conjugate fluxes and forces for these transport and rate processes from eq 9 are summarized in Table 1. The relationship between the heat flux \mathbf{J}_q and the conduction heat flux \mathbf{J}_u is $\mathbf{J}_q = \mathbf{J}_u - \sum_{i=1}^n \bar{h}_i \mathbf{J}_i$, which shows that heat flux can be expressed in various ways when diffusional fluxes are present within the system. Here \bar{h}_i is the partial specific enthalpy. The heat flux \mathbf{J}_q is also called the reduced heat flux and is the difference between the total heat flux and the heat flux due to diffusion.

Although Jaumann²³ derived the dissipation function, similar to eq 9, for various transport and rate processes in a system in 1911, it was unnoticed for sometime.^{2,6,20} The dissipation expression can include other processes; for example, for a current flux I the force is the electric potential difference divided by the absolute temperature, $\Delta E/T$.

In the dissipation phenomenological equations (DPE) approach,²⁴ eq 9 is used to identify a set of independent conjugate fluxes and forces to be used in the following linear phenomenological equations in the form of a conductance

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (10a)$$

or in the form of a resistance

$$X_i = \sum_{k=1}^n K_{ik} J_k \quad (10b)$$

where $K_{ik} = |L_{ik}|/|L|$, $|L|$ is the determinant of the matrix of the coefficients L_{ik} , and $|L_{ik}|$ is the minor for L_{ik} . The phenomenological coefficients L_{ik} or K_{ik} ($i, k = 1, 2, \dots, n$) are related to the transport coefficients, such as thermal conductivity and mass

diffusivity, can be functions of the local state parameters T and P , and the compositions, as well as the nature of the state, and can be determined experimentally.^{25,26} The resistance form of the phenomenological equations is preferred when the forces are difficult to determine or relate to measurable properties. The cross-coefficients L_{ik} , where $i \neq k$, describe the degree of coupling q_{ik} of processes within a system²⁷

$$q_{ik} = \frac{L_{ik}}{(L_{ii}L_{kk})^{1/2}} \quad (11)$$

Despite the linear phenomenological equations, the NET theory may lead to partial differential equations for the state variables that are nonlinear.^{4–6} Some of the reasons for this are (i) presence of convection term and quadratic source term in some of the balance equations, for example, energy equation, (ii) the nonlinear character of equation of state, and (iii) the dependence of phenomenological coefficients on the thermodynamic forces. To extend the range of applications of NET, Prigogine and Mazur⁴ introduced the notion of internal degrees of freedom. This gave rise to nonlinear (generally with respect to its process probability density) and linear Fokker–Planck equations, which are becoming increasingly popular, to describe nonequilibrium processes in internal coordinate space with NET theory's conventional rules.²⁸ The multivariate Fokker–Planck equation has a phenomenological parameter called the mobility matrix that relates thermodynamic forces to thermodynamic fluxes and may be derived from kinetic transport theory.^{29,30} With this new approach, it is shown that the evolution of hydrodynamic fluctuations in irreversible systems, as well as the Brownian motion of particles under nonuniform temperature conditions, can be described.^{28–32}

According to the Onsager reciprocal relations,^{17,18} the cross-coefficients are symmetric (i.e., $L_{ik} = L_{ki}$) for a set of independent conjugate fluxes and forces identified by the dissipation function or the entropy production. Onsager's relations are based on microscopic reversibility, which implies that the probability of a microscopic process proceeding in one direction is the same as that in the reverse direction;⁶ for example, for a simple reversible reaction, if one of several possible paths is preferred for the forward reaction, the same path must also be preferred for the reverse reaction. The Onsager reciprocal relations are independent of the state of a system or any other microscopic assumptions.^{1,6,21,25,26,33}

Equation 9 consists of three sums of products that are scalars of tensor rank zero, Ψ_0 , vectors with tensor rank one, Ψ_1 , and a tensor of rank two, Ψ_2 ; each of these must separately be greater than or equal to zero:

$$\Psi_0 = \tau(\nabla \cdot \mathbf{v}) - \sum_{j=1}^l J_{rj} A_j \geq 0 \quad (12)$$

$$\Psi_1 = \mathbf{J}_u \cdot T \nabla \left(\frac{1}{T} \right) + \sum_{i=1}^n \mathbf{J}_i \cdot \left[\mathbf{F}_i - T \nabla \left(\frac{\mu_i}{T} \right) \right] \geq 0 \quad (13)$$

$$\Psi_2 = \tau' : (\nabla \mathbf{v})' \geq 0 \quad (14)$$

where $\tau : (\nabla \mathbf{v}) = \tau' : (\nabla \mathbf{v})' + \tau(\nabla \cdot \mathbf{v})$ (the double dot product of a symmetric and antisymmetric tensor is zero). Another important part of NET is the Curie theorem,³⁴ which is a general symmetry principle that in isotropic macroscopic systems, a scalar process cannot produce a vectorial change, and vice versa. The Prigogine¹ interpretation of Curie's symmetry principle is that chemical affinity cannot cause a directed heat flux and more

generally that fluxes and forces whose tensorial rank differ by an odd number cannot couple in an isotropic medium. This is referred to as the Curie–Prigogine principle. However, such fluxes can be interrelated at the system boundaries (which are not isotropic) by the boundary conditions.

The fluxes in eq 9 can be defined in various ways; for example, definitions of mass fluxes change with the choice of reference velocity. However, the entropy production remains invariant under certain transformations;^{1,6} for example, for a system in mechanical equilibrium, $\sum_i (c_i \mathbf{F}_i - c_i \nabla \mu_i) = 0$ (from the isothermal Gibbs–Duhem equation and mechanical equilibrium equation), and the entropy production is invariant to the transformation $\mathbf{J}_i \rightarrow \mathbf{J}_i + \mathbf{v} c_i$, where \mathbf{J}_i is the mass flux, c_i is the concentration of component i , and \mathbf{v} is an arbitrary velocity. Furthermore, eq 13 can be transformed by introducing the total potential $\mu_i^* = \mu_i + \psi_i$, where ψ_i is the potential energy per unit mass, and the isothermal gradient of the total potential $\nabla_T \mu_i^*$, and replacing \mathbf{J}_u by the heat flux \mathbf{J}_q in $\mathbf{J}_u = \mathbf{J}_q + \sum_{i=1}^n \bar{h}_i \mathbf{J}_i$ with the following expression²¹

$$T \nabla \left(\frac{\mu_i}{T} \right) - \mathbf{F}_i = \nabla \mu_i - \mu_i \frac{\nabla T}{T} + \nabla \psi_i = \nabla_T \mu_i^* - \bar{h}_i \frac{\nabla T}{T} \quad (15)$$

where $\nabla \psi_i = -\mathbf{F}_i$. Then, for $n - 1$ independent diffusion fluxes, eq 13 becomes

$$\Psi_1 = -\mathbf{J}_q \cdot \nabla \ln T - \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \nabla_T (\mu_i^* - \mu_n^*) \geq 0 \quad (16)$$

Equations 12–16 are all in accord with the DEP approach.²⁴ If, however, the conjugate fluxes and forces are identified from the entropy production Φ and not by the dissipation function, then eqs 12–16 (divided by T) lead to different forms of thermodynamic forces. These various forms of forces and fluxes satisfy the principles of NET; they are all valid and therefore can be used to describe the transport and rate phenomena and coupling phenomena in phenomenological equations with a certain degree of usefulness under specific applications, such as membrane transport.^{1,4,6,22,35} This procedure eliminates an arbitrary choice of fluxes and forces and ensures that the cross-phenomenological coefficients obey the Onsager reciprocal relations.

Now we present some examples of identifying the fluxes and forces. The first example is of membrane transport. For isothermal, nonelectrolyte transport in an ideal binary system of solute (s) and water (w) through a membrane, the dissipation may be expressed in terms of chemical potential differences³⁵

$$\Psi = -J_s \Delta \mu_s - J_w \Delta \mu_w \geq 0 \quad (17)$$

Equation 17 leads to the following general forms of the fluxes:

$$J_s = -L_{ss} \Delta \mu_s - L_{sw} \Delta \mu_w \quad (18)$$

$$J_w = -L_{ws} \Delta \mu_s - L_{ww} \Delta \mu_w \quad (19)$$

where the forces $\Delta \mu_s$ and $\Delta \mu_w$ are the differences of chemical potentials across the membrane. According to the Onsager rules, $L_{sw} = L_{ws}$.

It would be convenient to replace the chemical potential in terms of other, more easily measurable quantities, such as $\Delta \mu_i = \bar{V}_i \Delta P + RT \Delta \ln c_i = \bar{V}_i \Delta P + RT \Delta c/c$, and express the dissipation in eq 17 as³⁵

$$\Psi = -J_s (\bar{V}_s \Delta P + \Delta \Pi/c_s) - J_w (\bar{V}_w \Delta P - \Delta \Pi/c_w) \geq 0 \quad (20)$$

Here J_s is the solute flux, and J_w is the water flux, while \bar{V}_s and \bar{V}_w are the partial volumes of the solute and the water, and c_s and c_w are the mean concentrations of solute and water, respectively, $\Delta\Pi$ is the osmotic pressure difference $\Delta\Pi = RT\Delta c_s$. By definition of the total volume flux, J_v , across the membrane as $J_v = J_w\bar{V}_w + J_s\bar{V}_s$ and the flux of the solute J_d relative to the water as $J_d = J_s/c_s - J_w/c_w$, eq 17 becomes

$$\Psi = -J_v\Delta P - J_d\Delta\Pi \geq 0 \quad (21)$$

With the conjugate forces of ΔP and $\Delta\Pi$, the commonly used phenomenological equations that describe the transport through a membrane are

$$J_v = -L_p\Delta P - L_{pd}\Delta\Pi \quad (22)$$

$$J_d = -L_{dp}\Delta P - L_d\Delta\Pi \quad (23)$$

From the Onsager reciprocity relations, $L_{pd} = L_{dp}$, the transport through the membrane can be described by three coefficients instead of four, which is desirable. The parameter L_p is the mechanical coefficient of filtration, L_d has the characteristics of a diffusion coefficient, the cross-coefficient L_{dp} is the ultrafiltration coefficient, and L_{pd} is the coefficient of osmotic flux. The ratio $-L_{pd}/L_p$ is called the reflection coefficient σ , which is always smaller than unity. For an ideal semipermeable membrane, $\sigma = 1$ since by definition such a membrane prevents the permeation of the solute.

The second example is diffusion of a single electrolyte and water in an ion-exchange membrane. The dissipation due to the flux of ions (1 and 2) from a neutral salt and water across the boundary is

$$\Psi = -J_1\Delta\bar{\mu}_1 - J_2\Delta\bar{\mu}_2 - J_w\Delta\mu_w \geq 0 \quad (24)$$

where $\bar{\mu}_i$ is the electrochemical potential of ion i and is expressed by $\bar{\mu}_i = \mu_i + z_iFE$; here z_i is the charge, and F is the Faraday constant. For a pair of electrodes interacting reversibly with one of the ions in the solution, the electromotive force ΔE can be related to the electrochemical potential difference of the i th ion, $\Delta E = \Delta\bar{\mu}_i/(z_iF)$. Equation 24 can be transformed to use the flux of neutral salt J_s and the electric current flux I . Assuming that the ion 2 reacts reversibly with the electrode and since ion 1 is not produced or consumed, then the flux of ion 1 is the flux of salt and is given by $J_s = J_1/\nu_1$, where ν_1 is the number of ions decomposed from each molecule of salt, which obeys the electroneutrality condition, $\nu_1z_1 + \nu_2z_2 = 0$. With the electric current flux $I = F(J_1z_1 + J_2z_2)$, eq 24 becomes

$$\Psi = -J_s\Delta\mu_s - J_w\Delta\mu_w - I\Delta E \geq 0 \quad (25)$$

It may be advantageous for certain cases to transform eq 25 further by using the volume flux J_v (eq 21) instead of water flux J_w and by introducing the relationships $\Delta\mu_s = \bar{V}_s\Delta P + \Delta\Pi/c_s$ for a nonelectrolyte solute and $\Delta\mu_w = \bar{V}_w(\Delta P - \Delta\Pi_s)$ into³⁵

$$\Psi = -J_v(\Delta P - \Delta\Pi_s) - J_s\Delta\Pi_s/c_s - I\Delta E \geq 0 \quad (26)$$

The related phenomenological equations are then

$$J_v = -L_{vv}(\Delta P - \Delta\Pi_s) - L_{vs}\Delta\Pi_s/c_s - L_{ve}\Delta E \quad (27)$$

$$J_s = -L_{sv}(\Delta P - \Delta\Pi_s) - L_{ss}\Delta\Pi_s/c_s - L_{se}\Delta E \quad (28)$$

$$I = -L_{ev}(\Delta P - \Delta\Pi_s) - L_{es}\Delta\Pi_s/c_s - L_{ee}\Delta E \quad (29)$$

Here the coefficients to characterize the membrane are six

instead of nine due to Onsager's reciprocal relations. These six coefficients can be determined experimentally, for example, by measuring conductivity of a membrane, transport numbers, and the fluxes due to electro-osmotic, osmotic, diffusional, and pressure.

In another example of identifying fluxes and forces, we consider heat and diffusion fluxes in a fluid under mechanical equilibrium with no chemical reaction, for which the dissipation is²²

$$\Psi = T\Phi = -\mathbf{J}_q \nabla \ln T - \sum_{i,k=1}^{n-1} \mathbf{J}_i \cdot a_{ik} \left[\sum_{j=1}^{n-1} \left(\frac{\partial \mu_k}{\partial w_j} \right)_{T,P,w_{i \neq j}} \nabla w_j \right] \geq 0 \quad (30)$$

where $a_{ik} = \delta_{ik} + w_k/w_i$, δ_{ik} is the unit tensor, and \mathbf{J}_i is the diffusion flux of component i . For a binary liquid mixture, a set of independent forces identified from the dissipation expression of eq 30 for heat and mass fluxes is $X_q = -\nabla \ln T$ and $X_1 = -1/w_2 (\partial \mu_1 / \partial w_1)_{T,P} \nabla w_1$, respectively. The phenomenological equations are then

$$-\mathbf{J}_q = L_{qq} \nabla \ln T + L_{q1} \frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1} \right)_{T,P} \nabla w_1 \quad (31)$$

$$-\mathbf{J}_1 = L_{1q} \nabla \ln T + L_{11} \frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1} \right)_{T,P} \nabla w_1 \quad (32)$$

Here, by the Onsager reciprocal relations, the matrix of phenomenological coefficients in eqs 26 and 27 is symmetric $L_{1q} = L_{q1}$. Since the dissipation function is positive, the phenomenological coefficients must satisfy the inequalities $L_{qq} > 0$, $L_{11} > 0$ and $L_{qq}L_{11} - L_{q1}^2 > 0$. Equations 26 and 32 along with eq 11 enable us to estimate the degree of coupling from the measured values of L_{ik} at various compositions and temperatures.^{26,36}

From the DPE approach,²⁴ for example, heat flux is expressed by

$$\mathbf{J}_q = -L_{qq} \nabla \ln T = -L_{qq} T \nabla \left(\frac{1}{T} \right) \quad (33)$$

After comparison with Fourier's law, $\mathbf{J}_q = -k \nabla T$, where k is the thermal conductivity, the phenomenological coefficient L_{qq} is

$$k = L_{qq}/T \quad (34)$$

Similarly, for mass flux \mathbf{J}_1 , we obtain

$$\mathbf{J}_1 = -L_{11} \left(1 + \frac{\nu_1 c_1}{\nu_2 c_2} \right) \left(\frac{\partial \mu_1}{\partial c_1} \right) \nabla c_1 \quad (35)$$

where c_i is the concentration of component i . Comparing with Fick's law $\mathbf{J}_1 = -D_1 \nabla c_1$, the phenomenological coefficient L_{11} is

$$L_{11} = D_1 \left[\left(1 + \frac{\nu_1 c_1}{\nu_2 c_2} \right) \left(\frac{\partial \mu_1}{\partial c_1} \right) \right]^{-1} \quad (36)$$

where D_1 is the diffusion coefficient of component 1.

The distribution of irreversibilities in the various parts of the process has led to the equipartition principle³⁷ that for a specified duty, the optimum operation of, for example, a heat exchanger or separator has uniformly distributed entropy production. Assuming a steady-state heat flux with no momentum and mass

transfer and constant thermal conductivity, the expression of total entropy production is from eq 30

$$\Phi = -\int_V L X^2 dV = -k \int_V \left(\frac{\nabla T}{T} \right)^2 dV \quad (37)$$

where the heat flux has been obtained from Fourier's law. Equation 37 shows that the entropy production is a function of the temperature field. Then the minimization problem is to obtain the temperature field, $T(x)$, corresponding to a minimum of Φ using the following Euler–Lagrange equation

$$\Phi - \sum \frac{d}{dx} \left(\frac{\partial \Phi}{\partial T} \right) = 0 \quad (38)$$

With minimization of entropy production function with the constraint of a specified heat load, eq 38 becomes

$$\sum \left[\frac{1}{T} \left(\frac{\partial T}{\partial x} \right)^2 - \frac{\partial T}{\partial x^2} \right] = 0 \quad (39)$$

For a heat exchanger, a characteristic direction related to the temperature field is $Z(x)$ normal to the heat transfer area, and eq 39 yields

$$\frac{\partial}{\partial x} \left[\frac{1}{T} \frac{\partial T}{\partial x} \right]_{Z(x)} = 0 \quad (40)$$

and we obtain

$$\left(\frac{\nabla T}{T} \right)_{Z(x)} = \text{constant} \quad (41)$$

Equation 41 shows that by keeping the driving force $\nabla T/T$ uniformly spatially distributed, the entropy production will be minimum.³⁷ Later studies on the equipartition principle have discussed the uniform distribution of forces in separation and reaction systems.^{38–45}

For an elementary chemical reaction, the flux J_r is

$$J_r = r_f (1 - e^{-A/(RT)}) \quad (42)$$

where the affinity A is expressed in terms of forward, r_f , and backward, r_b , reaction rates

$$A = RT \ln \frac{r_f}{r_b} \quad (43)$$

as well as in terms of chemical potential; for example, for a chemical reaction of $Y + B \leftrightarrow 2D$, affinity is

$$A = \mu_Y + \mu_B - 2\mu_D \quad (44)$$

Close to thermodynamic equilibrium, where $A/(RT) \ll 1$, we can expand eq 42 as

$$J_r = r_{f,eq} \frac{A}{RT} \quad (45)$$

which is to be compared with the linear phenomenological equations for chemical reactions

$$J_{ri} = \sum_{j=1}^l L_{ij} A_j \quad (46)$$

to obtain the phenomenological coefficient as

$$L_{ij} = \frac{r_{f,eq}}{RT} \quad (47)$$

At equilibrium, we have $r_{f,eq} = r_{b,eq}$, and the affinity vanishes.

An evolution criterion for dissipative processes^{6,12,13} can be obtained from the rate of change of volumetric entropy production, $P = \int \sum J X dV > 0$, and is expressed by

$$\frac{dP_i}{dt} = \frac{d}{dt} \left(\frac{d_i S}{dt} \right) = \int_V \left(\sum J_k \frac{dX_k}{dt} \right) dV + \int_V \left(\sum X_k \frac{dJ_k}{dt} \right) dV = \frac{d_X P_i}{dt} + \frac{d_J P_i}{dt} \quad (48)$$

Using the linear phenomenological equations and the Onsager reciprocal relations yields

$$\sum J_k dX_k = \sum L_{jk} X_j dX_k = \sum X_j d(L_{jk} X_k) = \sum X_j dJ_k \quad (49)$$

So, for systems close to global equilibrium only, we have

$$\frac{d_X P_i}{dt} = \frac{d_J P_i}{dt} \quad (50)$$

Outside the stationary state, for a dissipative system that is far from global equilibrium, we have

$$\frac{d_X P_i}{dt} \leq 0 \quad (51)$$

Equation 51 is independent of the type of phenomenological relations and shows that the entropy production decreases; but it does not indicate how the state will evolve. For example, the time-independent constraints may lead to states oscillating in time, such as Lotka–Volterra interactions. NET studies have shown that concentration oscillations are not inconsistent with the thermodynamic laws,⁶ and the NET theory can describe such systems and also the dynamics of an autocatalytic system,⁴⁶ such as Belousov–Zhabotinsky concentration oscillations.

The relations $P_i > 0$ and $d_X P_i < 0$ are the Lyapunov conditions for the stability of a state. The fundamental quantity that determines the stability is the excess volumetric entropy production $P(\delta S) = \int \sum \delta J \delta X dV \geq 0$, where (δS) is the perturbation in entropy. The sign of the excess entropy production determines the stability condition explicitly. The stability condition for a reaction in a uniform system at rest is given by the perturbation of the chemical affinities and of the corresponding reaction rates⁶

$$P(\delta S) = \frac{\sum_i \delta J_{r,i} \delta A_i}{T} \geq 0 \quad (52)$$

This section has shown that the linear NET approach is based on the following four postulates: (i) global forms of the flux–force relations are linear; (ii) in an isotropic system according to the Curie–Prigogine principle no coupling of fluxes and forces occurs if the tensorial order of the fluxes and forces differs by an odd number; (iii) in an isotropic system any flux is caused by all of the forces that satisfy the Curie–Prigogine principle, and any force is caused by all of the fluxes; the fluxes and forces are linearly dependent on each other, and the proportionality constants in these equations are the phenomenological coefficients; (iv) the matrix of the phenomenological coefficients

is symmetric provided that the conjugate fluxes and forces are identified from a dissipation function or an entropy production equation.

The Utility of Nonequilibrium Thermodynamics

Wei¹⁹ stated “IT has no useful theory, and brings no useful outcome neither for an engineer nor for a scientist; has nothing useful to say about irreversibility in general...IT seeks to describe a system by macroscopic thermodynamic variables and supposed to be true for any molecular structure and mechanism; it is a first-level theory, which is phenomenological in nature with unsatisfactory depth of penetration in our understanding of nature; it seeks merely to describe and correlate raw data, like curve fitting; it has no a priori estimates of the valid region of its laws.”

Let us examine these contentions. IT provides the working equations for nonequilibrium systems that are maintained through a flux of energy and matter. In the last five decades, the theory of linear NET has been developed and refined for systems in the linear region where the global form of flux–force relations are linearized, while for those systems far away from global equilibrium, the theory of extended nonequilibrium thermodynamics, which does not use the assumption of local equilibrium, and other approaches have been developed. In the linear region, all systems subject to external fluctuations experience an increase in entropy production and due to irreversible processes evolve to stationary states in which the entropy production is minimized. However, fluctuations in the nonlinear region can cause complex behavior such as Bénard cells and chemical oscillations controlled by hydrodynamics, mass transfer rates or reaction or other kinetic parameters. It is possible to identify the thermodynamic conditions under which far-from-equilibrium systems evolve to a new structured state.⁶

The second law of thermodynamics and the Gibbs chemical equilibrium principle determine the direction, but not the rate of a process. On the other hand, linear NET theory provides a linear relation between the rate of reaction J_r and the thermodynamic driving force, which in this case is the affinity of reaction A ($A = -\sum \nu_i \mu_i$, where the ν_i are the stoichiometric coefficients, which are positive for products and negative for reactants, and μ_i are the chemical potentials) when $|A| < RT \approx 2\text{--}6$ kJ/mol, where R is the universal gas constant and T is the absolute temperature. In the common temperature interval of 200–1000 K, this constraint is very restrictive for chemical reactions, while it is generally satisfied for transport processes with fast internal relaxation times, such as heat transfer and mass transfer, which are related to the gradients of $(1/T)$ and $-(\mu_i/T)$ (under mechanical equilibrium), respectively.^{1–6,8,23} The use of internal coordinate space in chemical reactions systems extends the range of applicability of NET;²⁸ for example, the use reaction coordinate as an internal variable within the NET theory may lead to the Arrhenius expression. This growing trend has been elaborated earlier.

For enzyme-catalyzed and chemical reactions, under certain boundary conditions, force–flux relationships can be described by a simple hyperbolic-tangent function,^{47–50} for example, the Michaelis–Menten equation, which is a nonlinear relation between the reaction rate and the substrate concentration but can be approximated as linear in some regions. Therefore, at very high positive and negative values of the affinity, reaction flux is almost independent of affinity, and there exists a quasilinear region between them, which extends over ~ 7 kJ/mol in the near equilibrium region.⁵¹ So the range of applicability of LNET is known.

Here we present some specific examples of utilizing the theory of NET with linear force–flux relations that may lead to nonlinear partial differential equations for the state variables. We start with a distillation column. Since a large amount of heat is required in the reboiler and a similar amount of heat is discharged at the condenser, a distillation column resembles a heat engine and will have an optimum operating condition. The thermodynamic optimization of a distillation column should lead to producing a more uniform distribution of irreversibility. This may be achieved through the column modifications, such as feed condition, feed stage location, and use of intermediate exchangers to reduce irreversibilities in sections with large driving forces and to increase irreversibility in sections with small driving forces.

The dissipation function per unit volume in a binary distillation is given by

$$\Psi = -\mathbf{J}_q \nabla \ln T - \sum_i \mathbf{J}_i \nabla \mu_{i,T} \quad (53)$$

where J_q is the heat and J_i are the mass fluxes of two components and $\nabla \mu_{i,T} = \nabla \mu_i^c$ at constant pressure. Using the Gibbs–Duhem equation, we can relate the chemical potentials of the heavy, h, and light, l, components in the gas phase as $\nabla \mu_h^c = -(y_l/y_h) \nabla \mu_l^c$ where y_l and y_h are the mole fractions in the gas phase of the light and heavy components. From eq 53, the entropy production is expressed by

$$\Phi = -\mathbf{J}_q \frac{\nabla T}{T^2} - \mathbf{J}_d y_l \frac{\nabla \mu_l}{T} \quad (54)$$

where \mathbf{J}_d (in $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$) is the relative mass flux across the interface $\mathbf{J}_d = (J_l/y_l) - (J_h/y_h)$. The phenomenological equations that follow from eq 54 are³⁹

$$\mathbf{J}_q = -L_{qq} \frac{\nabla T}{T^2} - L_{qd} y_l \frac{\nabla \mu_l}{T} \quad (55)$$

$$\mathbf{J}_d = -L_{dq} \frac{\nabla T}{T^2} - L_{dd} y_l \frac{\nabla \mu_l}{T} \quad (56)$$

where L_{qd} is the local phenomenological coefficient related to thermal conductivity and mass diffusivity and is known or can be determined from experiment.

The total rate of entropy production for a stage is obtained by integrating over the transport path between liquid and vapor

$$\Phi = \int_V \Phi_v dV \quad (57)$$

The entropy production rate is determined using quasi-steady-state calculations assuming the following constant gradient in the gas phase on each stage $\nabla T = \Delta T/\Delta x$ and $\nabla \mu_l = \Delta \mu_l/\Delta x$ with y_l and T approximately constant:

$$\Phi = -\frac{1}{T^2} \frac{\Delta T}{\Delta x} \int \mathbf{J}_q dV - \frac{y_l}{T} \frac{\Delta \mu_l}{\Delta x} \int \mathbf{J}_d dV \quad (58)$$

where $dV = dA dx$, A is the contact area, and x is the transfer distance on the stage. The expressions inside the integrals are the heat and mass fluxes per unit time in the mixture on a stage, respectively. This entropy production distribution in the column may help identify useful modification to reduce the entropy production.^{40,41}

For a separation process, the energy efficiency based on the second law of thermodynamics may be defined as

$$\eta = \frac{W_{\min}}{W_{\min} + W_{\text{lost}}} \quad (59)$$

where W_{\min} is the minimum work for the required separation over a reversible path. The reversible operation is the limiting case and is achieved when the forces vanish. In a steady-state distillation, heat and mass transfer are coupled, and if the temperature field or chemical potential is specified in the column, the other force would be fixed. A maximum second law efficiency may be obtained by minimizing the entropy production rate (and hence the rate of lost work production) with respect to one of these forces. A uniform entropy production rate corresponds to either minimum energy costs for the required separation and transfer area or minimum investment for a specified energy cost and leads to the thermodynamically optimum design and operation.³⁹ In absorption, desorption, membrane separation, and rectification, the major irreversibility is due to the mass transfer. If the mass transfer is optimum, the conditions on the concentration profiles provide the minimal irreversibility leading to a minimum in energy consumption. Analysis of a sieve tray distillation column reveals that the irreversibility on the tray is mostly due to the vapor–liquid interaction on the tray, and mass transfer is the largest contributor to the irreversibility.^{45,52,53}

We now consider chemically reacting systems. The local entropy production of a reacting mixture in a system with gradients in temperature T and chemical potentials μ_i is given by^{42,43}

$$\Phi = -\mathbf{J}_q \nabla \ln T - \sum_i \mathbf{J}_i \nabla \mu_{i,T} - \sum_j J_{r,j} A_j \quad (60)$$

Here, J_q is the total heat flux, J_i is the mass flux of component i , and $J_{r,j}$ is the scalar reaction rate (flux) of reaction j . Equation 60 leads to the following linear phenomenological equations

$$J_{r,k} = - \sum_j L_{kj} A_j \quad (61)$$

Consider a reactor with variations in temperature and compositions throughout but at mechanical equilibrium $\nabla P = 0$ and in which homogeneous reaction occurs. We will consider this reactor to consist of a large number of n subsystems of equal volume, each of uniform composition and temperature, and with the same reaction occurring. The reaction rate in the subsystem k is J_k , and the driving force is A_k , which is equal to Gibbs' free energy, ΔG_k . For a specified total reaction rate $\sum J_k V_k = -\sum L_k(A_k) V_k = \text{constant}$, the following entropy production is to be minimized:

$$\Phi = \sum_k \Phi_k V_k = \sum_k L_k(A_k)^2 V_k \quad (62)$$

The Cauchy–Lagrange method of constant multipliers yields

$$\frac{\partial \sum_m \Phi_m}{\partial(A_k)} + \lambda \frac{\partial \sum_m J_m}{\partial(A_k)} = 2L_k(A_k) + \lambda L_k = 0 \quad (63)$$

and

$$A_k = -\frac{\lambda}{2} \quad (64)$$

Equation 64 implies that for a given total reaction rate and a given total reactor volume, the minimum entropy production is obtained when the driving force A for the reaction is equal in all n subsystems. This result is independent of local variations in the reaction rate. Another consequence of eq 64 is that if we arrange the n subsystems in time instead of in space, then the collection of subsystems constitutes the reaction trajectory of a batch reactor. For a specified conversion within a specified time and with a minimum total entropy production, the sum given in eq 57 is then minimized. The result also implies the equipartition of forces. Similarly, the maximum total conversion is obtained for a given entropy production and reactor time when the driving force A is uniform.^{43,44}

Generally in a chemical reaction there is a nonlinear relation between the rate J_r and the driving force, and similar analyses exist for optimum operation.⁴⁴ Chemical reactors are often designed to operate at the maximum rate of reaction. An alternative path to that is a reactor operated with the minimum loss of useful work. The driving force that gives the maximum reaction rate for a specified total entropy production rate implies the driving force that gives minimum lost work for a total production J . Any reduction in lost work can result in economic gain, since it will change the energy, investment, and labor costs. So it may be useful to undertake energy optimization studies separately from economical analyses.

We can expect minimum lost work by equipartition of forces when the reaction enthalpy varies little with composition and if the reaction rate is a linear function of the conjugate force.⁴² Development of a particular operating path for a reactor with a specific output requires knowledge of reaction kinetics. The path that gives the minimum lost work is the compromise between energy efficiency and production rate for a given reactor. It may be financially advantageous to increase the reactor investment and lower the energy cost for the same product or to lower the production rate for a given energy input. In one example, it has been reported that a considerable (30%) reduction in the lost work can be achieved by lowering the production by only slightly (5%).⁴²

In the NET analysis of chemical reactions, the overall rate of reaction is expressed in terms of the chemical potential rather than concentration as is usually done in chemical kinetics. When the reaction system is far from equilibrium, the rate J_r may be proportional to a new affinity A^* defined as⁵⁴

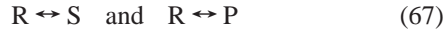
$$J_r = \epsilon_{ij} A^* = \epsilon_{ij} (e^{\mu_i/(RT)} - e^{\mu_j/(RT)}) \quad (65)$$

where ϵ_{ij} is a “reduced” rate constant or permeability of the potential barrier and does not depend on the thermodynamic parameters of the reactants; it is dependent on the transient state between the reactant groups i and j ; hence, $\epsilon_{ij} = \epsilon_{ji}$. In kinetic irreversibility, the rate of any backward elementary reaction is negligible compared with the rate of forward reaction, which corresponds to $\mu_i \gg \mu_j$. In this case, the rate of entropy production is expressed as a quadratic function of the force A^*

$$\Phi = \sum_{ij} \epsilon_{ij} A^{*2} \quad (66)$$

Equation 66 is related to the power dissipation and is compatible with the Prigogine theorem on the evolution of a dynamic system to the steady state.⁵⁴

As an example, consider the following two catalytic reactions



occurring through a joint intermediate RK



The dissipation and the linear phenomenological equations describing this system can be obtained from eqs 9 and 10 and are given by

$$\Psi = J_{r,s}A_{RS}^* + J_{r,p}A_{RP}^* \quad (69)$$

$$J_{r,s} = L_{11}A_{RS}^* + L_{12}A_{RP}^* \quad (70)$$

$$J_{r,p} = L_{21}A_{RS}^* + L_{22}A_{RP}^* \quad (71)$$

where the forces are

$$A_{RS}^* = (e^{\mu_R/(RT)} - e^{\mu_S/(RT)}) \quad (72)$$

$$A_{RP}^* = (e^{\mu_R/(RT)} - e^{\mu_P/(RT)}) \quad (73)$$

The phenomenological coefficients are

$$L_{11} = \frac{\epsilon_1\epsilon_2 + \epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}A_K^*, \quad L_{22} = \frac{\epsilon_1\epsilon_3 + \epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}A_K^*, \quad \text{and} \quad L_{12} = L_{21} = -\frac{\epsilon_2\epsilon_3}{\epsilon_1 + \epsilon_2 + \epsilon_3}A_K^* \quad (74)$$

Equation 74 shows that the phenomenological coefficients are dependent on the values of $(e^{\mu_i/(RT)})$, which differs from the linear phenomenological coefficients that are treated as constants. Equations 69–71 can be used for coupled complex chemical systems with unknown mechanisms that are described with phenomenological coefficients. The sign of the thermodynamic force A indicates the direction in which the system evolves. Interestingly, the second law of thermodynamics allows the dissipation of some of these reactions to decrease, for example, $J_{r,s}A_{RS}^* < 0$ but only if they are coupled with one or more other reactions with a larger positive dissipation, that is, $J_{r,p}A_{RP}^* \gg 0$, thus producing a positive total dissipation. This can have important implications in describing the organized states of coupled processes in complex systems, such as biological energy conversion cycles.^{13,14,50}

Another example of the use of NET theory comes from biological systems. Experiments and empirical analyses of cellular processes show that linear relations exist between the rate of respiration and growth rate in many microbial systems and for some of the steps in oxidative phosphorylation.^{55–72} Experiments also show that linearity between fluxes and forces characterizes transepithelial active Na^+ and H^+ transport and oxidative phosphorylation in mitochondria.⁷³ Pioneering work on the NET formulation of complex biological systems was done Kedem and Caplan,²⁷ Katchalsky and Curran,³⁵ Stucki,^{57,58} and Caplan and Essig.⁵⁰ In mitochondria, the respiration system is coupled to the oxidative phosphorylation, and the electrochemical potential gradient of protons across the inner membrane drives the synthesis of ATP from ADP and phosphate. The theory of NET has been used to describe the thermodynamic coupling and how the mitochondria can control the efficiency of oxidative phosphorylation by maximizing ATP production, the cellular phosphate potential, or the cost of ATP production.

For this coupled system, a representative dissipation expression is^{50,57,77}

$$\Psi = J_oX_o + J_pX_p \geq 0 \quad (75)$$

where the input force X_o is the redox potential of oxidizable substrates and X_p is the output force representing the phosphate potential, $X_p = -[\Delta G_p^o + RT \ln(c_{\text{ATP}}/c_{\text{ADPCP}})]$, which drives the ATP utilizing functions in the cell. The associated input flux J_o is the net oxygen consumption, and the out flux J_p is the net rate of ATP production.

Based on eq 75, the linear phenomenological relations are

$$J_p = L_pX_o + L_{po}X_p \quad (76)$$

$$J_o = L_{op}X_o + L_pX_p \quad (77)$$

Here L_o is the influence of substrate availability on oxygen consumption (flux); L_p is the feedback of the phosphate potential on ATP production (flux). The cross-coupling coefficient L_{op} is the phosphate influence on oxygen flux, while L_{po} shows the substrate dependency of ATP production. Experiments have established that the Onsager reciprocal relations hold for oxidative phosphorylation, that is, $L_{op} = L_{po}$.^{50,57,77}

The efficiency of such a coupled system of respiration (driving) and oxidative phosphorylation (driven) is defined as the output power (representing a decreasing dissipation as the synthesis of ATP is an endothermic process) divided by the input power^{43,50,68}

$$\epsilon = -\frac{J_pX_p}{J_oX_o} \quad (78)$$

By dividing eq 76 by eq 77 and by further dividing the numerator and denominator by $X_o(L_oL_p)^{1/2}$, we obtain

$$\epsilon = jx = -\frac{x + q}{q + 1/x} \quad (79)$$

where

$$j = \frac{J_p}{J_oZ}, \quad x = \frac{X_pZ}{X_o}, \quad Z = \left(\frac{L_p}{L_o}\right)^{1/2}$$

The ratio J_p/J_o is the conventional phosphate-to-oxygen consumption ratio, P/O, the term Z is called the phenomenological stoichiometry,⁵⁰ and the thermodynamic coupling q is²⁷

$$q = \frac{L_{op}}{(L_oL_p)^{1/2}} \quad 0 < |q| < 1 \quad (80)$$

Equation 79 shows the efficiency in terms of the force ratio x and the degree of coupling q . Coupling leads to a flux without its conjugated thermodynamic force or a flux in the direction opposite to the direction imposed by its thermodynamic force. Coupling leads to a decrease in the entropy production for an irreversible process if it is coupled to another irreversible process to yield an overall increase in the entropy production and may lead to an organized state or a dissipative structure, which continuously exchanges mass and energy with the outside, such as biological systems or Bénard convection cells or tornados.

For this biphasic function, given in eq 79, optimal thermodynamic efficiency ϵ_{opt} can be defined in terms of the degree of coupling and is given by^{50,57,77}

$$\epsilon_{\text{opt}} = \left(\frac{q}{1 + \sqrt{1 - q^2}} \right)^2 \quad (81)$$

The sequence of coupling is controlled at switch points where the mobility, specificity, and the catalysis of the coupling protein are altered in some specific ways, such as shifted equilibrium or regulated rates of conversion, between one protein state and another. An altered state of the protein is an intermediate in the coupled pathway.^{78–80} Equations 76–81 can only offer a phenomenological description of the coupled processes of respiration to oxidative phosphorylation, and NET does not present or require a detailed mechanism of the coupling.

When the transmembrane proton gradient vanishes, there is no longer a mechanism for coupling the energy output to the energy production, and eq 77 becomes

$$(J_o)_{\text{uncoupled}} = L_o X_o \quad (82)$$

When there is no ATP production (called the static head, sh, in bioenergetics), one can calculate the value of X_p from eq 76 and substitute it into eq 77 to obtain

$$(J_o)_{\text{sh}} = L_o X_o (1 - q^2) \quad (83)$$

The combination of eqs 82 and 83 leads to a relationship between the degree of coupling q and the measurable flux quantities

$$q = \left(1 - \frac{(J_o)_{\text{sh}}}{(J_o)_{\text{uncoupled}}} \right)^{1/2} \quad (84)$$

The thermodynamic approach summarized above has been used to quantify oxidative phosphorylation capacity in mitochondria,^{57–59,77} to incorporate photosynthesis into the NET description of enzymatic processes,⁸¹ and for the description of transport in membranes⁸² and biomembranes.⁸³ Such an analysis could be a basis to describe the maintenance of life and the ontogenic and phylogenic evolution of living systems.⁸⁴ In this approach, it is assumed that cells optimize their free energy production and utilization by lowering their entropy production at steady state, and this leads to the evolution of biological processes.^{50,77} A NET approach has been used recently as a basis for describing molecular evolution and for sequence and structure relations in proteins.^{85,86}

Some important biological processes resemble macroscopic machines governed by the action of molecular complexes; the concept of pumps have been used to understand the transport of ions and molecules across biological membranes, whereas the word motor is used in describing the transduction of chemical energy into mechanical work by proteins. Some of these systems have been studied with the NET approach.^{87–89}

Also a metabolic flux analysis combined with a metabolic control analysis has been used to quantify in vivo measurements of pathway fluxes in to and out of the cell and to identify the alternative pathways for the same chemical change.⁹² The flux control coefficients (FCC), C_i , quantify the influence of individual reaction rates on the overall flux through the pathway. For a linear pathway with n enzyme steps, the FCCs are given by

$$C_i = \frac{\partial \ln J_r}{\partial \ln J_{r,i}} \quad i = 1, \dots, n \quad (85)$$

where J_r is the steady-state flux through the pathway and $J_{r,i}$ is the rate of the i th enzyme reaction. The FCCs are related to the so-called elasticity coefficients through connectivity theorems

$$\sum_{i=1}^n \epsilon_j^i C_i = 0 \quad j = 2, \dots, n \quad (86)$$

where the elasticity coefficients are given by

$$\epsilon_j^i = \frac{\partial \ln J_{r,i}}{\partial \ln x_j} \quad i = 1, \dots, n; \quad j = 2, \dots, n \quad (87)$$

where x_j is the concentration of the j th metabolite. The elasticity coefficients can be determined using the NET theory, in which the kinetics of enzyme reactions are described as linear functions of the change in Gibbs free energy of the reaction.⁹² For example, for a simple two-step pathway, the elasticity coefficients can be related to the affinity of the reactions as has been shown for the first two reactions in the penicillin biosynthetic pathway. This approach determines the elasticity coefficients and the FCCs without a detailed kinetic model containing a large number of parameters.

Returning now to the electrolyte transport through an ion-exchange membrane, the thermodynamic efficiency of energy conversion ϵ from eq 17 can be defined as

$$\epsilon = \left(-\frac{J_s \Delta \mu_s}{I \Delta E} \right) + \left(-\frac{J_w \Delta \mu_w}{I \Delta E} \right) \quad (88)$$

where $I \Delta E$ represents the driving process and $J_s \Delta \mu_s$ and $J_w \Delta \mu_w$ are the driven processes. The three degrees of coupling are the ion–water coupling, q_{sw} , ion–current coupling, q_{se} , and water–current coupling, q_{we} , and are expressed by

$$q_{\text{sw}} = \frac{L_{\text{sw}}}{(L_{\text{ss}} L_{\text{ww}})^{1/2}}, \quad q_{\text{se}} = \frac{L_{\text{se}}}{(L_{\text{ss}} L_{\text{ee}})^{1/2}}, \quad \text{and} \quad q_{\text{we}} = \frac{L_{\text{we}}}{(L_{\text{ww}} L_{\text{ee}})^{1/2}} \quad (89)$$

For electrokinetic effects across a membrane with volume flux J_v , the dissipation function can be obtained from eq 20 when osmotic pressure vanishes ($\Delta \Pi = 0$)^{35,48,92}

$$\Psi = -J_v \Delta P - I \Delta E \quad (90)$$

This dissipation function leads to the linear relations

$$J_v = -L_{\text{vp}} \Delta P - L_{\text{pe}} \Delta E \quad (91)$$

$$I = -L_{\text{ep}} \Delta P - L_{\text{ee}} \Delta E \quad (92)$$

The efficiency for electrokinetic energy conversion for electroosmosis ($-J_v \Delta P / (I \Delta E)$) and for the streaming potential ($-I \Delta P / (J_v \Delta P)$) can be expressed in terms of the degree of coupling, and the optimum efficiency is⁹³

$$\epsilon_{\text{opt}} = \frac{\sqrt{1 + \beta} - 1}{\sqrt{1 + \beta} + 1} \quad (93)$$

where β is related to the degree of coupling

$$\beta = \left(\frac{1}{q^2} - 1 \right)^{-1} \quad (94)$$

Equation 93 is similar to eq 81.

Extended Nonequilibrium Thermodynamics

The classical linear diffusion and heat conduction laws of Fick and Fourier generally are not useful in describing processes that are far from global equilibrium, for example, diffusion of

polymers, and fluxes through porous media in which the fluxes and forces are not linearly related. A formulation with a larger range of applicability is needed; one such formalism is extended nonequilibrium thermodynamics, another is called the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC), and both are based on the NET theory.^{93–100}

In binary ideal diffusion without heat transfer and viscous effects, the natural state variables would be the mass density and velocities, ρ_1 , ρ_2 , v_1 , and v_2 . An alternative set could be, for example, the total mass density, $\rho = \rho_1 + \rho_2$, the concentration of component 1, $c_1 = \rho_1/\rho$, the barycentric velocity, $v = (\rho_1 v_1 + \rho_2 v_2)/\rho$, and the mass diffusion flux, $J = \rho_1(v_1 - v)$. In the extended NET formulation, the classical and conserved variables of ρ , c , and v , as well as the nonconserved flux variables, are used. Extended nonequilibrium thermodynamics uses the evolution equations for the conserved variables, that is, the usual balance equations of mass, concentration, and momentum, and for the dissipative fluxes J ; therefore, it can describe a larger class of phenomena. The resulting equation using the procedure that has been detailed by Depireux and Lebon⁹⁴ leads to nonlinear and non-Fickian mass diffusion. This type of equation is useful in describing diffusion in polymers, in which the viscous stress and diffusion are coupled.

In the GENERIC formulation, the balance equations are generated using total energy and total entropy as potentials and the independence of the reversible part of the process from its irreversible one on a macroscopic level,^{97,99} though the balance equations contain reversible and irreversible parts. In another method, an extended nonequilibrium thermodynamics formulation has been used with time derivatives of the usual thermodynamic properties as additional variables for the heat transfer problem.⁹⁸ These are some examples illustrating that the field of thermodynamics is being developed to cover a much larger region of transport phenomena using various approaches, such as the notion internal degrees of freedom.^{28–32}

The introduction of the concept of internal degrees of freedom into NET extends its range to describe a wider class of nonequilibrium processes and also leads to Fokker–Planck equations,²⁹ as elaborated before. In this approach, fluctuations of thermodynamic variables are considered as internal degrees of freedom, and therefore, the fluctuation theory is integrated into NET.^{28,31,32} This approach introduces the distribution function in the space of fluctuating thermodynamic variables and the Gibbs' entropy postulate and deals with very slow changes compared to the microscopic time scale.²⁸ Frank^{28,29} derived generalized multivariate Fokker–Planck equations by using kinetic transport theory and linear NET for multiparticle systems and showed that Fokker–Planck equations can describe relaxation processes and stationary solutions that differ from the usual Boltzmann distributions.

Rational thermodynamics, another method, provides a means of deriving constitutive equations without assuming the local equilibrium hypothesis.^{95,97} In this formulation, absolute temperature and entropy do not have a precise physical interpretation, and it is assumed that the system has a memory and that the behavior of system at a given time is determined by the characteristic parameters of both the present and the past. However, the general expressions for the balance of mass, momentum, and energy are still used. Still another method is network thermodynamics, based on the NET formulation, which can be used in both the linear and nonlinear regions. It has the flexibility to deal with the systems in which the transport and reactions are occurring simultaneously, either at steady or unsteady state.^{101–104}

While there is not yet a single formulation for all systems, this summary shows that nonequilibrium thermodynamics is still being developed and has been applied to a large collection of problems in the chemical, physical, and biological sciences.

Conclusions

All real processes are irreversible and produce entropy. NET based on local equilibrium determines the rate of entropy production in irreversible systems regardless of their distances from the global equilibrium. The entropy production is the sum of the product of fluxes and forces operating in each process within a system, and the classification of forces and fluxes are not unique but a matter of convention. Some main disadvantages of NET are the following: (i) validity of it is rather limited for chemical reactions, (ii) practical applications are mainly limited to systems in the linear regime where the global form of flux–force relations are linear, (iii) it cannot describe the detailed mechanism of a process, (iv) it cannot determine the phenomenological coefficients, which are related to the transport properties of a process, and (v) it cannot suggest the ways of minimizing the entropy production within a system. However, NET also has many advantages, and some of these are as follows: (i) NET is applicable to transport processes with the fast relaxation times such as heat and mass fluxes, momentum flux, electric current, and others. It has also applications for chemical reactions close to global equilibrium with linear region on the reaction velocity versus affinity plot. However, the theory of NET with linear thermodynamic force–flux relations yields partial differential equations, which are nonlinear for the state variables; generally many systems are close to equilibrium locally, although they may be far from equilibrium globally; therefore, NET applicability is not limited to systems close to global equilibrium only. (ii) It can be used to interrelate the fluxes caused by all forces present and forces caused by all fluxes within a system. (iii) It can describe the coupling phenomena between the processes within a system through the nonvanishing cross-coefficients of the phenomenological equations. (iv) NET can describe the stability of nonequilibrium systems and dissipative structures with coupled phenomena. (v) NET does not need the detailed or mechanistic knowledge of the process in its formulation. (vi) NET determines the entropy production and relates the irreversibility to the lost work; the level of lost work is a measure of thermodynamic imperfection of a particular engineering process and operation. (vii) NET uses the second law of thermodynamics to relate the irreversibility into the entropy production and coupling to irreversible phenomena and hence emphasizes the role of the second law in thermodynamically optimum design and in coupled processes. (viii) Onsager's reciprocal relations reduce the number of unknown proportionality constants for cases of multiple fluxes and forces. (ix) Finally, partial differential equations obtained from NET can provide a unified approach in developing physical, biological, and engineering sciences, such as hydrodynamics, biophysics, and biochemistry; it can also be used to describe transport and rate processes, separation, coupled processes, organized structures, and other processes in physical and biological systems. Since equilibrium implies the death of a living cell, NET formulation provides a useful tool for studying the biological systems, biological self-organization, and other dissipative systems.

Nomenclature

a : parameter in eq 30.

A : affinity, contact area.

A_j : chemical affinity of reaction j .
 A^* : affinity for reaction in nonlinear region.
 Be : Bejan number.
 c : concentration.
 C : flux control coefficient.
 D : diffusion coefficient.
 E : electric potential.
 F : force per unit mass.
 G : Gibbs' free energy.
 \bar{h} : partial specific enthalpy.
 j : ratio of fluxes.
 J_i : diffusion flux of component i .
 k : thermal conductivity.
 L_{ik} : phenomenological coefficient (conductance).
 n : number of components, number of subsystems.
 N_k : number of moles density of component k .
 q : degree of coupling.
 q : heat flux.
 P : pressure, rate change of volumetric entropy production.
 r : reaction rate.
 R : universal gas constant.
 J_r : reaction velocity (flux).
 S : entropy.
 $d_e S$: entropy change between system and its surroundings.
 $d_i S$: entropy production within a system.
 t : time.
 T : absolute temperature.
 u_i : partial specific internal energy of component i .
 v : velocity.
 V : volume.
 \bar{V} : partial molar volume.
 w : mass fraction.
 W : work.
 x : ratio of forces, distance.
 X_i : thermodynamic force.
 Y : gas-phase concentration.
 Z : phenomenological stoichiometry.
 $Z(x)$: direction normal to the heat transfer area.

Greek Symbols

δ : unit tensor.
 ϵ : thermodynamic efficiency, reduced rate constant.
 η : second law efficiency.
 μ_i : chemical potential of component i .
 ν : stoichiometric coefficients, number of ions dissolving from molecule.

Π : osmotic pressure.

ρ : density.

τ : shear stress.

Φ : entropy production.

ψ : potential energy.

Θ : viscous dissipation function.

Ψ : dissipation function.

Subscripts

b,f: backward and forward, respectively.

eq: equilibrium.

h: heavy.

i,j,k : components.

l: light.

min: minimum.

o: oxygen.

opt: optimum.

p: phosphate.

q: heat.

s: solvent.

sh: static head.

u: energy.

w: solvent.

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