Coupling refers to a flux occurring without its primary thermodynamic driving force; for example, mass flux without a concentration gradient called the thermal diffusion is a well-known coupled process. Coupling also refers to a flux occurring in a direction opposite to the direction imposed by its driving force; for example, a mass flux can occur from a low to a high concentration region and is called the active transport or uphill transport, such as potassium and sodium pumps coupled to chemical energy released by the hydrolysis of adenosine triphosphate (ATP) in biological systems. Although the coupled processes seem to be in conflict with the principles of second law of thermodynamics, interestingly, the second law allows the progress of a process against its driving force and hence with a decrease in entropy $\Delta S_j < 0$, but only if it is coupled with another process with larger positive entropy change, $\Delta S_k >> 0$, thus producing a positive total entropy change $(\Delta S_j + \Delta S_k) > 0$. This is consistent with the second-law statement that a finite amount of organization may be obtained at the expense of a greater amount of disorganization in a series of coupled spontaneous processes. This can have important implications in describing the coupled phenomena and organized structures in complex systems, such as biological energy conversion cycles.(1-7)

Some examples of coupled processes follow. Thermoelectric phenomena have the Seebeck and the Peltier effects; in the Seebeck effect, a temperature difference between two junctions of dissimilar metals produces an electromotive force; in the Peltier effect, the two junctions are maintained at the same constant temperature, and a current applied through the system causes a heat flux from one junction to another. The uniform junction temperatures are maintained under a steady heat flux.(1)

In heat and mass transfer, thermal diffusion (Soret effect) and the Dufour effect are the coupled transport processes. In the Soret effect, a mass flux occurs due to a temperature gradient without a corresponding concentration gradient, while in the Dufour effect, a heat flux occurs due to chemical potential gradient, without temperature gradient. Thermal diffusion is a critical separation process for isotope mixtures and is of great interest in oceanographic problems. Another well-known coupled process is the Bénard instability where a critical temperature gradient in a fluid induces a structured convection in the forms of cells or rotated flows (left and right) and contributes to an effective coupling between hydrodynamic and thermal forces.(12) In living systems, the respiration system is coupled to the oxidative phosphorylation, and ATP is produced.(4,5,7) The change from a simple to a complex behavior is the order and coherence within a system that leads to coupled processes and organized dissipative structures.(1-3) Such structures are not necessarily far from local equilibrium and can only be maintained by a constant supply of mass and/or energy fluxes. They have long been confined only to biological systems, but this is changing and researchers from diverse disciplines are studying the occurrences and implications of coupled processes.(2,3,13)

Teaching of coupled processes in a first-year graduate class should cover the approximate contents presented in Table 1, which also lists some possible textbooks and their present coverage. Textbooks for transport phenomena by Bird, et al.(8) and Deen(9) describe some of the coupled phenomena without the nonequilibrium thermodynamic (NET) theory, while the texts for thermodynamics by Kondepudi and Prigogine,(1) and Demirel(10) describe some of the coupled transport and reaction processes with the postulates and formulations of NET. The concept of nonequilibrium systems and the NET theory would provide students with the basic fundamentals of coupling (see Table 2). This study presents the use of NET in teaching various coupled processes from physical and biological systems in the transport phenomena II graduate course at Virginia Tech.
NONEQUILIBRIUM SYSTEMS

Transport and rate processes are open, nonequilibrium, and irreversible systems with temperature, concentration, pressure gradients, and affinities. Figure 1 shows a stationary-state nonequilibrium system with coupled and uncoupled fluxes. Although the system is not at global equilibrium, thermodynamic properties such as temperature, concentration, pressure and internal energy are well-defined in an elemental volume surrounding a given point. These volumes are small enough that the substance in them can be treated as uniform, and yet they contain a sufficient number of molecules so that the principles of statistics and the methods of phenomenological thermodynamics are applicable. Therefore a local equilibrium in any elemental volume exists, and the thermodynamic properties are related to the state variables in the same manner as in equilibrium. Mostly, the internal relaxation processes in the fluid or material are much faster than the rate of change imposed upon the state variables, and the local equilibrium concept is valid for a wide range of transport and rate processes of usual fluid systems. For example, the relaxation time for heat conduction for gases at normal conditions is $10^{-12}$s, and for typical fluids $10^{-11}$-$10^{-13}$ s. Local equilibrium is not valid in highly rarefied gases where collisions are too infrequent, however, and hence the relaxation times are much higher. The extension of equilibrium thermodynamics to nonequilibrium systems with the local equilibrium assumption is possible in terms of entropy $s[T(x), n_i(x)]$ and energy $u[T(x), n_i(x)]$ densities, which are a function of the temperature and species 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 system

$$S = \int_V s[T(x), n_i(x)] dV$$

$$U = \int_V u[T(x), n_i(x)] dV$$

and using the $s(x)$ and $u(x)$, we obtain the local variables of

$$\left(\frac{\partial s}{\partial u}\right)_{n_i} = 1/T(x)$$

$$\left(\frac{\partial s}{\partial n_i}\right)_u = -\mu(x)/T(x)$$

The level of distance from the global equilibrium may be treated as a parameter of a process, and is called the thermodynamic branch as shown in Figure 2. Near global equilibrium, there are linear relations between the driving forces in the process and the fluxes that result; examples are Fourier’s and Fick’s laws. Processes occurring far from global equilibrium, however, such as most chemical reactions, lead to nonlinear force-flux relations, and in some cases to the sponta-

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<td>Local equilibrium</td>
<td>Ch 19</td>
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neous formation of self-organized dissipative structures.\(^1,4-6\)

**NONEQUILIBRIUM THERMODYNAMICS (NET)**

Change of total entropy of a system is

\[
\frac{dS}{dVdt} = \frac{dS}{dVdt} + \frac{dS}{dVdt} \tag{1}
\]

where the \(dS/dVdt\) is the rate change of total entropy, 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 due to irreversible processes within a system, and is always positive. We determine the volumetric rate of entropy production

\[
\Phi = \left( \frac{dS}{dVdt} \right) = \sum J_k X_k \geq 0
\]

or the rate of local dissipation of Gibbs free energy in terms of a product of a flux, \(J_k\), and a thermodynamic force, \(X_k\).

\[
\Psi = \sum J_k X_k = \Phi \geq 0
\]

For a multicomponent fluid system with \(n\) species and \(z\) number of chemical reactions, the dissipation function can be derived by incorporating the entropy balance into the general balance equations of mass, momentum, and energy, and the Gibbs relation\(^7,10\)

\[
- \sum_j J_{ij} \frac{d\mu_j}{dt} + \frac{1}{T} \sum_j \left( \frac{d\mu_j}{dt} \right)_T = \frac{1}{T} \sum_{j=1}^{z} A_{ij} \sum_{j} J_{r,j}\geq 0
\]

In Eq. (2), the dissipation function consists of four separate contributions of heat transfer, mass transfer, momentum transfer, and chemical reactions (without electrical and magnetic effects); their conjugate fluxes and forces are summarized in Table 3. The relationship between the heat flux, \(J_q\), and the conduction heat flux, \(J_q'\), is

\[
J_q = J_q' + \sum_{i=1}^{n} \tilde{h}_i J_i
\]

where \(\tilde{h}_i\) is the partial specific enthalpy.

In the dissipation-phenomenological equation (DPE) approach,\(^12\) Eq. (2) identifies a set of independent conjugate fluxes and forces to be used in the following linear phenomenological equations in the form of a conductance formulation

\[
J_i = \sum_{k=1}^{m} L_{ik} X_k \tag{3}
\]

If the fluxes are easy to determine or relate to measurable properties, then the following resistance formulation is preferred

\[
X_i = \sum_{k=1}^{m} K_{ik} J_k \tag{4}
\]

The phenomenological coefficients, \(L_{ik}\) or \(K_{ik}\) (\(i,k = 1,2,...,m\)) are related to the transport coefficients, such as thermal conductivity, \(k\), and mass diffusivity, \(D\), and can be determined experimentally; \(K_{ik} = ||L_{ik}/||L||\) is the determinant of the matrix of the coefficients \(L_{ik}\), and \(||L||\) is the minor for \(L_{ik}\). According to Onsager’s reciprocal relations, the cross coefficients are symmetric \(L_{ik} = L_{ki}\); (\(i\neq k\)) for a set of independent conjugate fluxes and forces identified by the dissipation function or the rate entropy production. Onsager’s relations are based on microscopic reversibility, and are independent of the state of a system or any other microscopic assumptions.\(^1,10\) The cross coefficients, \(L_{ik}\), describe the degree of coupling, \(q_{ik}\), of processes\(^4,12\)

Table 3

<table>
<thead>
<tr>
<th>Process</th>
<th>Flux</th>
<th>Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat flux</td>
<td>(J_q = \sum \tilde{h}_i J_i)</td>
<td>(\tilde{h}_i = TV\left( \frac{1}{T} \right))</td>
</tr>
<tr>
<td>Mass flux</td>
<td>(J_q = \sum \tilde{h}_i J_i)</td>
<td>(X_i = TV\left( \frac{\mu_j}{T} \right))</td>
</tr>
<tr>
<td>Viscous effect</td>
<td>(J_q = \sum \tilde{h}_i J_i)</td>
<td>(X_v = TV\left( \frac{\mu_j}{T} \right))</td>
</tr>
<tr>
<td>Reaction velocity</td>
<td>(J_q = \sum \tilde{h}_i J_i)</td>
<td>(X_i = TV\left( \frac{\mu_j}{T} \right))</td>
</tr>
</tbody>
</table>

Figure 2. Thermodynamic branch indicating the linear and nonlinear regions; \(X\) shows the force and \(X_c\) is the critical force or distance from equilibrium state, where no force exists. After a critical distance from global equilibrium the system may move to an organized structure that needs constant supply of matter and/or energy.

**TABLE 3**

Conjugate Fluxes and Forces Identified by the Dissipation Function (DPE) Approach\(^12\)

<table>
<thead>
<tr>
<th>Process</th>
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<tr>
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</tr>
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</table>

where

\[
TV\left( \frac{\mu_j}{T} \right) = TV\left( \frac{\mu_j}{T} \right) + h_i TV\left( \frac{1}{T} \right)
\]
\[ q_{ik} = \frac{L_{ik} - L_{ik}}{(L_{ik})^{1/2}} \] (5)

which can be determined using the transport coefficients.\(^{(12,13,16)}\)

From Eqs. (2) and (3), the dissipation is expressed by

\[ \Psi = \sum_{m} L_{ik} X_{ik} X_{k} \geq 0 \]

and the matrix form of it shows that the dissipation function is quadratic in form

\[ \Psi = X^T L X = J^T K J \geq 0 \]

for all forces and fluxes, where \( X^T \) and \( J^T \) are the transpose of the respective vectors. Table 4 shows the four main postulates in the linear NET approach.

**COUPLED TRANSPORT AND RATE PROCESSES**

Equation (2) consists of scalars of tensor rank zero \( \Psi_0 \), vectors with tensor rank one \( \Psi_1 \), and a tensor of rank two \( \Psi_2 \)

\[ \Psi_0 = \tau(\nabla \cdot \mathbf{v}) - \sum_{ij} J_{ij} \cdot \mathbf{A}_{ij} \geq 0 \] (6)

\[ \Psi_1 = \mathbf{J}_a T \left( \frac{1}{T} \right) + \sum_{i=1}^{n} \mathbf{J}_i \left[ F_i - T \left( \frac{\partial \rho}{\partial T} \right) \right] \geq 0 \] (7)

\[ \Psi_2 = \tau : (\nabla \mathbf{v})^T \geq 0 \] (8)

where \( \tau(\nabla \mathbf{v}) = \tau(\nabla \mathbf{v})^{\text{sym}} + \tau(\nabla \mathbf{v})^{\text{asym}} \) (the double dot product of a symmetric and antisymmetric tensor is zero). According to the Curie-Prigogine principle, in isotropic macroscopic systems, a scalar process cannot produce a vectorial change and vice versa; for example chemical affinity cannot cause a directed heat flux, and more generally, fluxes and forces whose tensorial rank differ by an odd number cannot couple in an isotropic medium. Such fluxes can be coupled at the system boundaries (which are not isotropic) by the boundary conditions, however.

The fluxes and forces in Eq. (2) can be defined in various ways, for example, definitions of mass fluxes change with the choice of reference velocity. The entropy production remains invariant under certain transformations, however;\(^{(11,14)}\) for example, for a system in mechanical equilibrium

\[ \sum (c_i F_i - c_i \mu_j) = 0 \]

(from the isothermal Gibbs-Duhem equation and mechanical equilibrium equation), and for the transformation

\[ \mathbf{J}_i \rightarrow \mathbf{J}_i + \mathbf{v} \mathbf{c}_i \]

where \( \mathbf{c}_i \) is the concentration of component \( i \), and \( \mathbf{v} \) is an arbitrary average velocity. Equation (7) can be transformed further by introducing the total potential

\[ \mu_i = \mu_i + \Psi_i \]

where \( \Psi \) is the specific potential energy, the isothermal gradient of the total potential \( \nabla T \mu_i \) and the heat flux \( \mathbf{J}_q \) in the following expression

\[ TV \left( \frac{\mu_i}{T} \right) - F_i = \nabla T \mu_i - \frac{\mathbf{V} T}{T} \mu_i = \nabla T \mu_i - \frac{\mathbf{V} T}{T} \mu_i \] (9)

where \( \nabla \Psi_i = - F_i \). Using Eq. (9) in Eq. (7), we have for \( n-1 \) independent diffusion fluxes

\[ \Psi_i = - \mathbf{J}_q \nabla \ln T - \sum_{i=1}^{n-1} \mathbf{J}_i \nabla T (\mu_i^* - \mu_i^*) \geq 0 \] (10)

This procedure eliminates an arbitrary choice of fluxes and forces, and ensures that the cross phenomenological coefficients obey the Onsager’s relations for linear phenomenological laws.

In the next section, some examples of transport and rate processes from physical and biological systems are presented to show the utility of NET in teaching coupled processes.

**Heat and Mass Transfer**

For a fluid under mechanical equilibrium with no chemical reaction, the dissipation function of heat and independent diffusion fluxes from Eq. (10) is\(^{(7,12,14)}\)

\[ \Psi = - J_q \nabla \ln T - \sum_{i=1}^{n} \mathbf{J}_i a_{ik} \left[ \sum_{j=1}^{n-1} \left( \frac{\partial h_k}{\partial W_j} \right)_{T,P,W_{i+1}} \nabla W_j \right] \geq 0 \] (11)

where \( a_{ik} = \delta_{ik} + \frac{w}{w}, \) and \( \delta_k \) is the unit tensor, \( w_j \) is the mass fraction of species \( j \). In a binary liquid mixture, a set of independent forces identified by the dissipation function of Eq. (11) for heat and mass fluxes is \( X_i = - \nabla \ln T \) and \( X_j = -(1/w) \partial \mu_j / \partial W_{ij} \) \( T, \mathbf{V}^w_{ij} \), respectively. Then the linear phenomenological equations are

\[ -J_q = L_{qf} \ln T + L_{qf} \left( \frac{\partial h_j}{\partial W_j} \right)_{T,P} \nabla W_j \] (12)

---

**TABLE 4**

Four Main Postulates of the Linear Nonequilibrium Thermodynamics (NET) Approach

- Global form of the flux-force relations is linear, and the proportionality constants in these relations are the phenomenological coefficients.
- 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.
- In an isotropic system, any flux is caused by all the forces that satisfy the Curie-Prigogine principle, and any force is caused by all the fluxes.
- Matrix of the phenomenological coefficients is symmetric provided that the conjugate fluxes and forces are identified from a dissipation function equation or an entropy production equation.
Here, by the Onsager reciprocal relations, \( L_{ii} = L_{qi} \). From Eq. (12), heat flux due to primary coefficient \( L_{ii} \) is expressed by \( J_q = -L_{qii} V \ln T = -L_{qii} T \ln(T_1/T) \); after comparing with Fourier’s law \( \dot{Q} = -kV \nabla T \), the \( L_{ii} \) is related to the thermal conductivity \( k \): \( L_{ii} = kT \). When no volume change occurs due to the diffusion flows (no volume flow), the mass flux \( J_i \) is:

\[
J_i = -L_{ii}(1 + \nabla c_i / \nabla c_j)(\partial \mu_i / \partial c_i)\nabla c_i
\]

where \( c_i \) and \( \nabla c_i \) are the concentration and partial molar volume of component \( i \), respectively; comparing it with Fick’s law, \( J_i = -D_i \nabla c_i \), the \( L_{ii} \) is related to the diffusion coefficient of component \( i D_i \); \( L_{ii} = D_i [1 + \nabla c_i / \nabla c_j (\partial \mu_i / \partial c_i)]^{-1} \).

The heat of transport \( Q \) of species \( i \) is defined by \( Q_i = L_{qii} \). It is an expression of the form of the second law of thermodynamics and can be measured experimentally. Equations (12) and (13) can be expressed in terms of heat of transport \( Q_i \) and the transport coefficients:

\[
-J_q = kVT + \rho D_q c_i \nabla c_i \tag{14}
\]

\[
-J_i = \rho D_{i1} V \ln T + \rho D_v \nabla c_i \tag{15}
\]

where \( D_{i1} \) is the thermal diffusion coefficient for species \( i \); \( D_v \) is the density. The second term on the right side of Eq. (14) shows the Soret effect, also known as thermal diffusion, while the first term on the right side of Eq. (15) shows the Dufour effect. Comparing Eqs. (13) and (15) with vanishing concentration gradients yields \( L_{qii} = \rho D_{i1} \). The degree of coupling can be expressed in terms of \( Q_i \) and the other transport coefficients from Eq. (5):

\[
q = Q_i \left( \rho D_i M_{i1} M_{aw} w_{w1} \ln c_i V c_i^2 \right)^{1/2} \tag{16}
\]

where \( M_i \) and \( M_{aw} \) show the molecular mass of species \( i \) and mixture, respectively, \( R \) is the gas constant, and \( \Gamma_{i1} = (\partial \ln \gamma_i / \partial \ln x_i)_{T,P} \) is called the thermodynamic factor, \( \gamma \) model. As heat and mass fluxes are both vectors, the sign of \( q \) indicates the direction of fluxes of a species; if \( q > 0 \), the flow of a species may drag another species in the same direction, while the flux may push the other species in the opposite direction if \( q < 0 \). Using Eqs. (14) to (16), effects of concentration and temperature on the coupled heat and mass fluxes in liquid mixtures can be studied.

**Membrane Transport** • The dissipation equation for an isothermal, nonelectrolyte transport in an ideal binary system of solute (s) and water (w) through a membrane is:

\[
\Psi = -J_s \Delta \mu_s - J_w \Delta \mu_w \geq 0 \tag{17}
\]

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

\[
J_s = -L_{sw} \Delta \mu_s - L_{sw} \Delta \mu_w \tag{18}
\]

\[
J_w = -L_{w} \Delta \mu_s - L_{sw} \Delta \mu_w \tag{19}
\]

where the forces \( \Delta \mu_s, \Delta \mu_w \) are the differences of chemical potentials, and \( J_s \) and \( J_w \) are the fluxes for the solute and water across the membrane, respectively. It is customary to replace \( \Delta \mu_i \) with more easily measurable quantities, such as \( \Delta \mu_i = \overline{\nabla i} \Delta P + R T \ln c_i = \overline{\nabla i} \Delta P + R T \Delta c / c_i \), and Eq. (17) becomes:

\[
\Psi = -J_s \Delta \mu_s - J_w \Delta \mu_w \geq 0 \tag{20}
\]

With the forces of \( \Delta P \) and \( \Delta \Pi \) identified by Eq. (21), the commonly used phenomenological equations that describe the transport through a membrane are:

\[
J_s = -L_{pd} \Delta P - L_{pd} \Delta \Pi \tag{22}
\]

\[
J_w = -L_{pd} \Delta P - L_{pd} \Delta \Pi \tag{23}
\]

With Onsager’s relations, \( L_{pd} = L_{dp} \), the transport through the membrane can be described by the three coefficients instead of four. The coefficient \( L_{pd} \) is the mechanical coefficient of filtration, \( L_{dp} \) 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 \( L_{dp}/L_{pd} \) is called the reflection coefficient \( \sigma \), which is always smaller than unity. With these coefficients, the degree of coupling is obtained from \( q = L_{dp}/L_{pd} \).

**Transport in Ion-Exchange Membrane** • For the diffusion of a single electrolyte and water in an ion-exchange membrane, the dissipation due to the fluxes of ions (1 and 2) from a neutral salt and water across the boundary is:

\[
\Psi = -J_1 \Delta \mu_1 - J_2 \Delta \mu_2 - J_w \Delta \mu_w \geq 0 \tag{24}
\]

where \( \overline{\nabla i} \) is the electrochemical potential of ion \( i \), and expressed by \( \overline{\nabla i} = \mu_i + z_i F E \); 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 \( \Delta \mathcal{E} \) can be related to the electrochemical potential difference of \( \mathcal{E} \) th ion \( \Delta \mathcal{E} = \Delta \overline{\nabla w} / z_i F \). By 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 given by \( J_1 = J_w / v_1 \), where \( v_1 \) is the number of ions decomposed per molecule of salt, which obeys the
electroneutrality condition \( \nu_{z_1} + \nu_{z_2} = 0 \). With the electric current flux \( I = \mathcal{F}(J_{z_1} + J_{z_2}) \), Eq. (24) becomes

\[
\Psi = -J_{\text{w}} \Delta \mu_{\text{w}} - J_{\text{sw}} \Delta \mu_{\text{sw}} - 1\Delta E \geq 0
\]  

(25)

It may be advantageous for certain cases to transform Eq. (25) further by using the volume flux \( J_v \) instead of water flux \( J_{\text{w}} \), and by introducing the relationships \( \Delta \mu_{\text{w}} = \nabla \Delta P / c_s \) for a nonelectrolyte solute and \( \Delta \mu_{\text{sw}} = \nabla (\Delta P - \Delta \Pi_{\text{sw}}) \) into

\[
\Psi = -J_v (\Delta P - \Delta \Pi_{\text{sw}}) - J_{\text{sw}} \Delta \Pi_{\text{sw}} / c_s - 1\Delta E \geq 0
\]  

(26)

The related phenomenological equations are then

\[
J_v = -L_{\text{sv}} (\Delta P - \Delta \Pi_{\text{sw}}) - L_{\text{sv}} \Delta \Pi_{\text{sw}} / c_s - L_{\text{sv}} \Delta E
\]  

(27)

\[
J_s = -L_{\text{sv}} (\Delta P - \Delta \Pi_{\text{sw}}) - L_{\text{sv}} \Delta \Pi_{\text{sw}} / c_s - L_{\text{sv}} \Delta E
\]  

(28)

\[
I = -L_{\text{sv}} (\Delta P - \Delta \Pi_{\text{sw}}) - L_{\text{sv}} \Delta \Pi_{\text{sw}} / c_s - L_{\text{sv}} \Delta E
\]  

(29)

In Eqs. (27) to (20) six coefficients characterize the membrane transport due to Onsager’s relations. The coefficients can be determined by measuring conductivity of the membrane, transport numbers, and the fluxes due to electro-osmotic, osmotic, diffusional, and pressure.

The thermodynamic efficiency of energy conversion \( \eta \) can be defined as

\[
\eta = - \frac{J_{\text{w}} \Delta \mu_{\text{w}}}{1\Delta E} - \frac{J_{\text{sw}} \Delta \mu_{\text{sw}}}{1\Delta E}
\]  

(30)

where \( 1\Delta E \) represents the driving process, and \( J_{\text{w}} \Delta \mu_{\text{w}} \) and \( J_{\text{sw}} \Delta \mu_{\text{sw}} \) are the driven processes. The degrees of coupling are the ion-current \( q_{\text{sw}} \), ion-current \( q_{\text{sc}} \), and water-current \( q_{\text{we}} \), which are

\[
q_{\text{sw}} = \frac{L_{\text{sw}}}{(L_{\text{sw}} L_{\text{ww}})^{1/2}} \quad q_{\text{sc}} = \frac{L_{\text{se}}}{(L_{\text{sw}} L_{\text{ce}})^{1/2}} \quad q_{\text{we}} = \frac{L_{\text{we}}}{(L_{\text{ww}} L_{\text{ce}})^{1/2}}
\]  

(31)

**Oxidative Phosphorylation (OP) •** Experiments and empirical analyses of cellular processes show that linear relations exist between the rate of respiration and growth rate in many organisms, and for some of the steps in OP\(^{(5,6,10)}\). In mitochondria, the respiration system is coupled to the OP, and the electrochemical potential gradient of protons across the inner membrane drives the synthesis of ATP from adenosine diphosphate (ADP) and phosphate (Pi). The theory of NET has been used to describe the thermodynamic coupling, and how the mitochondria can control the efficiency of OP by maximizing ATP production, the cellular phosphate potential, or the cost of ATP production.\(^{(5,6)}\) For this coupled system a representative dissipation expression is

\[
\Psi = J_o X_0 + J_p X_p \geq 0
\]  

(32)

where the input force \( X_0 \) is the redox potential of oxidizable substrates, and \( X_p \) is the output force representing the phosphate potential, \( X_p = [\Delta \Pi_{\text{po}} + RT \ln(\epsilon_{\text{ATP}} / \epsilon_{\text{ADP}^p\Pi})] \), which drives the ATP utilizing functions in the cell; \( \Delta \Pi_{\text{po}} \) is the standard Gibbs free energy. 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. (32), the linear phenomenological relations are

\[
J_p = L_{\text{po}} X_o + L_{\text{po}} X_p
\]  

(33)

\[
J_o = L_{\text{op}} X_o + L_{\text{op}} X_p
\]  

(34)

Here, \( L_o \) is the influence of substrate availability on oxygen consumption rate and \( L_p \) is the feedback of the phosphate potential on ATP production rate. The cross-coupling coefficient \( L_{\text{op}} \) is the phosphate influence on oxygen flux, while \( L_{\text{po}} \) shows the substrate dependency of ATP production. Experiments shows that Onsager’s reciprocal relations hold for OP, and \( L_{\text{op}} = L_{\text{po}} \).

Thermodynamic efficiency of the coupled systems of respiration (driving, \( \Psi >> 0 \)) and OP (driven, \( \Psi < 0 \)) is defined as the ratio of output power (\( \Psi_p = J_p X_p \)) to the input power (\( \Psi_o = J_o X_o \)),

\[
\eta = \frac{J_p X_p}{J_o X_o}
\]  

(35)

By dividing Eq. (33) by Eq. (34), and by further dividing the numerator and denominator by \( X_o L_o L_p \), we obtain the efficiency in terms of the force ratio \( x \) and the degree coupling \( q \)

\[
\eta = J_o X_0 \frac{x+q}{q+1/x}
\]  

(36)

where

\[
J_p = J_o Z x = X_p Z \frac{L_p}{L_o} \quad Z = \left( \frac{L_p}{L_o} \right)^{1/2}
\]  

and

\[
q = - \frac{L_{\text{opt}}}{L_o L_p} \quad 0 < q < 1
\]

The ratio \( J_p/J_o \) is the conventional phosphate-to-oxygen consumption ratio (P/O), the term \( Z \) is called the phenomenological stoichiometry. For the biphasic function in Eq. (36), optimal thermodynamic efficiency \( \eta_{\text{opt}} \) is the function of \( q \) only, as shown in Figure 3.

\[
\eta_{\text{opt}} = \frac{q}{1+\sqrt{1-q^2}}
\]  

(37)

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. Equations (32) to (37) offer a phenomenological description of respiration and oxidative phosphorylation, and the NET approach does not require a detailed mechanism of the coupling.

**Chemical Reactions •** NET theory provides a linear relation between the rate of reaction \( J \) and the affinity \( A \) of reaction \( A = -n v_{i} \mu_{i} \), where the \( v_{i} \) are the stoichiometric coefficients, which are positive for products and negative for
 reactants) when |AI| < RT ~ 2-6 kJ/mol. Obviously, in the common temperature interval of 200-1000 K this constraint is very restrictive for chemical reactions. The use of internal coordinate space in chemical reactions systems extends the range of applicability of NET, however, and yields nonlinear (generally with respect to its process probability density) and linear Fokker-Planck equations to describe nonequilibrium processes in internal coordinate space with NET theory's conventional rules. The multivariate Fokker-Planck equation has a phenomenological parameter called the mobility matrix that relates forces to fluxes and can be derived from kinetic transport theory; the equations can describe the evolution of hydrodynamic fluctuations in irreversible systems, as well as the Brownian motion of particles under nonuniform temperatures. The multivariate Fokker-Planck equation has a phenomenological parameter called the mobility matrix that relates forces to fluxes and can be derived from kinetic transport theory; the equations can describe the evolution of hydrodynamic fluctuations in irreversible systems, as well as the Brownian motion of particles under nonuniform temperatures. The micromorphic principle is approximately 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 quasi-linear region in between, which extends over an ~7 kJ/mol. For an elementary chemical reaction the flux Jr is

\[ Jr = r_f (1 - e^{-A/RT}) \]  

where the affinity A is expressed in terms of forward rf and backward rb reaction rates A = RT ln(rf/rb) as well as in terms of chemical potential. Close to thermodynamic equilibrium, dynamic variables and the Gibbs’ entropy postulate, and deals with nonequilibrium processes, and also leads to Fokker-Planck equations; fluctuations of thermodynamic variables are considered as internal degrees of freedom, and therefore the fluctuation theory is integrated into NET. 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. Figure 3. Change of efficiencies in terms of flux ratios and degree of couplings; for a maximal net rate of ATP flux at optimal efficiency: qf = 0.786, for an economic net ATP flux (JfXf)opt: qf = 0.953, for a maximal output power (JpXp)opt at optimal efficiency: qf = 0.910, and for an economic net output power (JpXp)opt: qf = 0.972.

\[
\rho C_p \frac{\partial T}{\partial t} = -V^T \left[ \rho \left( D_{BB} Q_B + D_{BP} Q_P \right) \nabla w_B + \rho \left( D_{PB} Q_B + D_{PP} Q_P \right) \nabla w_P + kV T \right] + (\Delta H_t) r_B
\]

where \( \Delta H_t \) is the heat of reaction. Eqs. (42) to (44) are the modeling equations that take into account the coupling between the two diffusion fluxes of the species B, P, and the heat flux with a set of suitable boundary and initial conditions. No couplings occur between the scalar reaction flux and the vectorial transport fluxes assuming that the medium is isotropic according to Curie-Prigogine principle.

**EXTENDED NONEQUILIBRIUM THERMODYNAMICS (NET)**

ENET uses the evolution equations for the conserved variables and therefore it can describe a larger class of phenomena. The resulting equations lead to nonlinear and non-Fickian mass diffusion, and can describe diffusion in polymers, in which the viscous stress and diffusion are coupled. 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; fluctuations of thermodynamic variables are considered as internal degrees of freedom, and therefore the fluctuation theory is integrated into NET. 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.
CONCLUSIONS

Coupled transport and rate processes are important part of some natural and complex phenomena. Partial differential equations obtained from the NET theory can provide a unified approach to describe coupled phenomena and organized structures and other processes in physical, chemical, and biological systems. Therefore, the NET formulations within a suitable graduate transport phenomena textbook may be useful to teach coupled transport and rate processes.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>affinity (J mol⁻¹)</td>
</tr>
<tr>
<td>c</td>
<td>concentration (mol m⁻³)</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient (m² s⁻¹)</td>
</tr>
<tr>
<td>Dₜ</td>
<td>thermal diffusion coefficient</td>
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<tr>
<td>E</td>
<td>electric potential (V)</td>
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<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>F*</td>
<td>force per unit mass (kg m s⁻² kg⁻¹)</td>
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<tr>
<td>G</td>
<td>Gibbs’ free energy (J)</td>
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<tr>
<td>H</td>
<td>heat of reaction (J mol⁻¹)</td>
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<tr>
<td>I</td>
<td>current flux</td>
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<tr>
<td>j</td>
<td>ratio of fluxes</td>
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<tr>
<td>Jₛ</td>
<td>heat flux (J m⁻² s⁻¹)</td>
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<tr>
<td>Jᵢ</td>
<td>mass flux for component i (kg m⁻² s⁻¹)</td>
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<tr>
<td>Jᵢₗ</td>
<td>reaction velocity (flux)</td>
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<tr>
<td>k</td>
<td>thermal conductivity (J m⁻² s⁻¹ K), reaction rate constant (s⁻¹), Kᵢₗ</td>
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<td>Lᵢₗ</td>
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<td>M</td>
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<td>Nᵢ</td>
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<td>P</td>
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<td>Qₘ</td>
<td>heat of reaction</td>
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<tr>
<td>r</td>
<td>reaction rate (mol s⁻¹)</td>
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<td>potential energy (J)</td>
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<tr>
<td>Ψ</td>
<td>dissipation function (J s⁻¹)</td>
</tr>
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</table>

Subscripts

- b,f: backward and forward respectively
- eq: equilibrium
- i,j,k: components
- o: oxygen
- opt: optimum
- p: phosphate
- q: heat
- s: solvent
- w: water

REFERENCES