TEACHING COUPLED TRANSPORT AND RATE PROCESSES

YASAR DEMIREL
Virginia Polytechnic Institute and State University • Blacksburg, VA 24061

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, *i.e.,* $\Delta S_k >> 0$, 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.(2) 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(7) 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.

Yasar Demirel *is a visiting professor in the Department of Chemical Engineering at Virginia Tech. He received his PhD from the University of Birmingham, UK. He teaches senior design, thermodynamics, transport phenomena, and simulation. His research focuses on coupled transport and rate processes in physical and biological systems. He is the author of a book titled* Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical and Biological Systems, *published by Elsevier, and over 90 journal articles and conference proceedings.*

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.(1,10) 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.(1,7-9) 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.(11) 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

$$S = \int_V s\left[T(x), n_i(x)\right]dV \qquad U = \int_V u\left[T(x), n_i(x)\right]dV$$

and using the s(x) and u(x), we obtain the local variables of(2-6)

$$\left(\partial s/\partial u\right)_{n_i} = 1/T(x) \quad \text{and} \quad \left(\partial s/\partial n_i\right)_u = -\mu(x)/T(x)$$

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.(1) 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-

TABLE 1
Contents and Coverage for Coupled Transport and Rate Phenomena

Contents	*Bird, Stewart & Lightfoot*[8]	*Kondepudi & Prigogine*[1]	*Deen*[9]
Nonequilibrium systems		Ch 1.2	
Local equilibrium	Ch 24.1	Ch 3.4, 15.1	
Dissipative structures		Ch 19	
Nonequilibrium thermodynamics		Ch 15	
Balance equations & entropy balance	Ch 19.2, 24.1	Ch 15.3	Ch 11.8
Dissipation (entropy production)	Ch 24.1, B7	Ch 15.2	Ch 11.8
Minimum entropy production		Ch 17.2	
Identification of fluxes and forces	Ch 24.3	Ch 15.5	
Phenomenological equations		Ch 16.1	Ch 11.4
Phenomenological coefficients		Ch 16.1	Ch 11.8
Onsager's reciprocal relations	Ch 24.1	Ch 16.2	Ch 11.4
Curie-Prigogine principle	Ch 24.1	Ch 16.2	
Degree of coupling			
Coupled systems			
Multicomponent diffusion	Ch 24.2, 22.9		Ch 11.8
Diffusion in electrolyte systems			Ch 11.7
Heat and mass transfer	Ch 24.2	Ch 16.8	Ch 11.4
Thermoelectric phenomena		Ch 16.3	
Chemical reactions		Ch 16.5	
Electrokinetic phenomena		Ch 16.7	
Membrane transport	Ch 24.5		
Biological systems		Ch 19.3, 19.6	
Second law analysis			
Lost work, exergy loss			
Extended nonequilibrium Thermodynamics			
Network thermodynamics			
Mosaic in nonequilibrium thermodynamics			
Rational thermodynamics			
Example problems & questions	Ch 24	Ch 15, 16	Ch 11.4

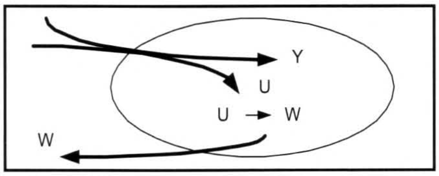

Figure 1. *Nonequilibrium distribution of components in a stationary-state coupled system: Flux of species U is coupled with the flux of Y through an enzyme in a cell. Species of Y do not take part in any chemical reaction. Neither the flux of U nor the flux of Y is coupled to the flux of W, however.*

TABLE 2
General Procedure for Teaching Coupled Phenomena with Nonequilibrium Thermodynamics Approach

<u>*Step*</u>	<u>*Procedure*</u>
1.	Start with the Gibbs relation in terms of the relevant thermodynamic variables
2.	Establish the conservation laws for the variables
3.	Establish an entropy balance equation and derive the rate of entropy production or dissipation function to identify a set of conjugate fluxes and thermodynamic forces
4.	Use these fluxes and forces in linear phenomenological equations
5.	Calculate total fluxes in terms of forces or forces in terms of driving forces
6.	Calculate the transport coefficients using Onsager's reciprocal rules
7.	Calculate the dissipations due to individual processes
8.	Quantify the effects and degree of coupling on transport and rate processes

neous formation of self-organized dissipative structures.(1,4-6)

NONEQUILIBRIUM THERMODYNAMICS (NET)

Change of total entropy of a system is

$$\frac{dS}{dVdt}=\frac{d_eS}{dVdt}+\frac{d_iS}{dVdt} \tag{1}$$

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

$$\Phi=\left(d_iS/dVdt\right)=\sum J_kX_k\geq 0$$

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,

$$\Psi=\sum J_kX_k=T\Phi\geq 0$$

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)

$$\Psi=\sum JX=T\Phi=$$

$$T\left\{\mathbf{J}_u\nabla\left(\frac{1}{T}\right)-\frac{1}{T}\sum_{i=1}^{n}\mathbf{J}_i\left[T\nabla\left(\frac{\mu_i}{T}\right)-\mathbf{F}_i\right]+\frac{1}{T}\tau:(\nabla v)-\frac{1}{T}\sum_{j=1}^{z}A_jJ_{r,j}\right\}\geq 0 \tag{2}$$

where

$\mathbf{J}_u$ and $\mathbf{J}_i$ vectors of heat and mass fluxes respectively
μ_i chemical potential of species i
$\mathbf{F}_i$ force per unit mass of component i
τ viscosity part of stress tensor
v velocity
A affinity ($A=-\sum\nu_i\mu_i$)
ν stoichiometric coefficients
J_r reaction flux, which is a scalar.

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, $\mathbf{J}_q$, and the conduction heat flux, $\mathbf{J}_u$, is

$$\mathbf{J}_q=\mathbf{J}_u-\sum_{i=1}^{n}\bar{h}_i\mathbf{J}_i$$

where $\bar{h}_i$ 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; $K_{ik}=|L|_{ik}/|L|$, |L| is the determinant of the matrix of the coefficients L_{ik}, and $|L|_{ik}$ is the minor for L_{ik}. According to Onsager's reciprocal relations, the cross coefficients are symmetric $L_{ik}=L_{ki}$; (i≠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)

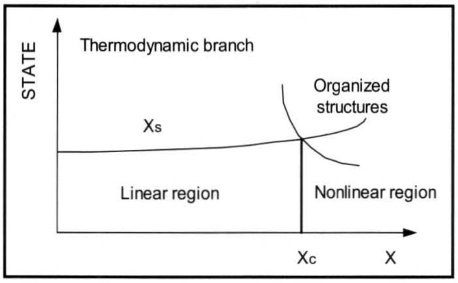

Figure 2. *Thermodynamic branch indicating the linear and nonlinear regions; X shows the force and Xc is the critical force or distance from equilibrium state, where no force exists. After a critical distance from global equilibrium the system may move to an organized structure that needs constant supply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

TABLE 3
Conjugate Fluxes and Forces Identified by the Dissipation Function (DPE) Approach[12]

Process	***Flux***	***Force***
Heat flux	$\mathbf{J}_u=L_qX_q$	$X_q=T\nabla\left(\frac{1}{T}\right)$
Mass flux	$\mathbf{J}_i=L_iX_i$	$X_i=F_i-T\nabla\left(\frac{\mu_i}{T}\right)$
Viscous effect	$\mathbf{J}_v=L_vX_v$	$X_v=(\nabla v)$
Reaction velocity	$J_r=L_rX_r$	$X_r=A_j=-\sum_{i=1}^{k}\mu_i\nu_{ij}$

where

$$\nabla\left(\frac{\mu_i}{T}\right)=\nabla\left(\frac{\mu_i}{T}\right)_T+h_i\nabla\left(\frac{1}{T}\right)$$

$$q_{ik} = \frac{L_{ik}}{\left(L_{ii} L_{kk}\right)^{1/2}} \tag{5}$$

which can be determined using the transport coefficients.(12,13,16)

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

$$\Psi = \sum_{i,k}^{m} L_{ik} X_i X_k \geq 0$$

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

$$\Psi = \mathbf{X}^T \mathbf{L} \mathbf{X} = \mathbf{J}^T \mathbf{K} \mathbf{J} \geq 0$$

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

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Equation (2) consists of scalars of tensor rank zero Ψ_0, vectors with tensor rank one Ψ_1, and a tensor of rank two Ψ_2

$$\Psi_0 = \tau(\nabla \cdot \mathbf{v}) - \sum_{j=1}^{z} J_{r,j} A_j \geq 0 \tag{6}$$

$$\Psi_1 = \mathbf{J}_u T \nabla\left(\frac{1}{T}\right) + \sum_{i=1}^{n} \mathbf{J}_i \left[\mathbf{F}_i - T\nabla\left(\frac{\mu_i}{T}\right)\right] \geq 0 \tag{7}$$

$$\Psi_2 = \boldsymbol{\tau}' : (\nabla \mathbf{v})'^{S} \geq 0 \tag{8}$$

where $\boldsymbol{\tau}:(\nabla \mathbf{v}) = \boldsymbol{\tau}':(\nabla \mathbf{v})' + \tau(\nabla \cdot \mathbf{v})$ (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.

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

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;(1,14) for example, for a system in mechanical equilibrium

$$\sum \left(c_i \mathbf{F}_i - c_i \nabla \mu\right) = 0$$

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

$$\mathbf{J}_i \rightarrow \mathbf{J}_i + \mathbf{v} c_i$$

where c_i is the concentration of component i, and **v** is an arbitrary average velocity. Equation (7) can be transformed further by introducing the total potential

$$\mu_i^* = \mu_i + \psi_i$$

where Ψ_i 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

$$T\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i = \nabla \mu_I - \mu_i \frac{\nabla T}{T} + \nabla \psi_i = \nabla_T \mu_i^* - \bar{h}_i \frac{\nabla T}{T} \tag{9}$$

where $\nabla \psi_i = -\mathbf{F}_i$. Using Eq. (9) in Eq. (7), we have for n-1 independent diffusion fluxes

$$\Psi_1 = -\mathbf{J}_q \nabla \ln T - \sum_{i=1}^{n-1} \mathbf{J}_i \nabla_T \left(\mu_i^* - \mu_n^*\right) \geq 0 \tag{10}$$

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)

$$\Psi = -\mathbf{J}_q \nabla \ln T - \sum_{i,k=1}^{n-1} \mathbf{J}_i a_{ik} \left[\sum_{j=1}^{n-1} \left(\frac{\partial \mu_k}{\partial w_j}\right)_{T,P,w_{i \neq j}} \nabla w_j\right] \geq 0 \tag{11}$$

where $a_{ik} = \delta_{ik} + w_k/w_n$, and δ_{ik} 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 $X_q = -\nabla \ln T$ and $X_1 = -(1/w_2)(\partial \mu_1/\partial w_1)_{T,P} \nabla w_1$, respectively. Then the linear phenomenological equations are

$$-\mathbf{J}_q = L_{qq} \nabla \ln T + L_{q1} \frac{1}{w_2} \left(\frac{\partial \mu_1}{\partial w_1}\right)_{T,P} \nabla w_1 \tag{12}$$

$$-\mathbf{J}_q = L_{1q}\nabla \ln T + L_{11}\frac{1}{w_2}\left(\frac{\partial \mu_1}{\partial w_1}\right)_{T,P}\nabla w_1 \qquad (13)$$

Here, by the Onsager reciprocal relations, $L_{1q} = L_{q1}$. From Eq. (12), heat flux due to primary coefficient L_{qq} is expressed by $\mathbf{J}_q = -L_{qq}\nabla \ln T = -L_{qq}T\nabla(1/T)$; after comparing with Fourier's law $\mathbf{J}_q = -k\nabla T$, the L_{qq} is related to the thermal conductivity $k: L_{qq} = kT$. When no volume change occurs due to the diffusion flows (no volume flow), the mass flux $\mathbf{J}_1$ is:

$$\mathbf{J}_1 = -L_{11}\left(1 + \overline{V}_1 c_1 / \overline{V}_2 c_2\right)\left(\partial \mu_1 / \partial c_1\right)\nabla c_1$$

where c_i and $\overline{V}_i$ are the concentration and partial molar volume of component i, respectively; comparing it with Fick's law, $\mathbf{J}_1 = -D_1\nabla c_1$, the L_{11} is related to the diffusion coefficient of component 1 D_1: $L_{11} = D_1\left[\left(1 + \overline{V}_1 c_1 / \overline{V}_2 c_2\right)\left(\partial \mu_1 / \partial c_1\right)\right]^{-1}$.

The heat of transport Q_1 of species 1 is defined by $Q_1 = L_{1q}/L_{11}$; it is the heat carried by a unit flux of species 1 when there is no temperature gradient and no diffusion of other species and can be measured experimentally.(15) Equations (12) and (13) can be expressed in terms of heat of transport Q_1 and the transport coefficients(7,12)

$$-\mathbf{J}_q = k\nabla T + \rho D_1 Q_1 \nabla w_1 \qquad (14)$$

$$-\mathbf{J}_1 = \rho D_{T,1}\nabla \ln T + \rho D_1 \nabla w_1 \qquad (15)$$

where $D_{T,1}$ is the thermal diffusion coefficient for species 1 and ρ 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 $L_{1q} = \rho D_{T,1}$. The degree of coupling can be expressed in terms of Q_1 and the other transport coefficients from Eq. (5) (13)

$$q = Q_1\left(\frac{\rho D M_1 M_2 w_1 w_2}{k M_{av} R T^2 (1+\Gamma_{11})}\right)^{1/2} \qquad (16)$$

where M_i and M_{av} show the molecular mass of species i and mixture, respectively, *R* is the gas constant, and $\Gamma_{11} = \left(\partial \ln \gamma_1 / \partial \ln x_1\right)_{T,P}$ is called the thermodynamic factor, and can be determined from experimental data or an activity coefficient, γ, 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 $q < 0$.(7,12) Using Eqs. (14) to (16), effects of concentration and temperature on the coupled heat and mass fluxes in liquid mixtures can be studied.(7,13)

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(14,16)

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

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

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

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

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 $\Delta\mu_i = \overline{V}_i\Delta P + RT\Delta \ln c_i = \overline{V}_i\Delta P + RT\Delta c / c$, and Eq. (17) becomes

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

where $\overline{V}_s$ and $\overline{V}_w$ are the partial volumes, c_s and c_w are the concentrations of solute and water, respectively, $\Delta\Pi$ is the osmotic pressure difference $\Delta\Pi = RT\Delta c_s$. Equation (20) is further transformed by defining the total volume flux J_v across the membrane as $J_v = J_w\overline{V}_w + J_s\overline{V}_s$, and the flux of the solute J_d relative to the water $J_d = J_s/c_s - J_w/c_w$

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

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

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

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

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_p is the mechanical coefficient of filtration, the 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. With these coefficients, the degree of coupling is obtained from $q = L_{dp}/(L_p L_d)^{1/2}$.

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(14,16)

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

where $\overline{\mu}_i$ is the electrochemical potential of ion i, and expressed by $\overline{\mu}_i = \mu_i + z_i F E$; 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 ΔE can be related to the electrochemical potential difference of the *i*th ion $\Delta E = \Delta\overline{\mu}_i / z_i F$. 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 $J_s = J_1/\nu_1$, where ν_1 is the number of ions decomposed per molecule of salt, which obeys the electroneutrality condition $\nu_1 z_1 + \nu_2 z_2 = 0$. With the electric current flux $I = F(J_1 z_1 + J_2 z_2)$, Eq. (24) becomes

$$\Psi = -J_s \Delta\mu_s - J_w \Delta\mu_w - I\Delta E \geq 0 \tag{25}$$

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

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

The related phenomenological equations are then

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

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

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

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 η can be defined as

$$\eta = \left(-\frac{J_s \Delta\mu_s}{I\Delta E}\right) + \left(-\frac{J_w \Delta\mu_w}{I\Delta E}\right) \tag{30}$$

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 degrees of coupling are the ion-water q_{sw}, ion-current q_{se}, and water-current q_{we}, which are

$$q_{sw} = \frac{L_{sw}}{(L_{ss}L_{ww})^{1/2}} \qquad q_{se} = \frac{L_{se}}{(L_{ss}L_{ee})^{1/2}} \qquad q_{we} = \frac{L_{we}}{(L_{ww}L_{ee})^{1/2}} \tag{31}$$

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.(5,6,16) 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

$$\Psi = J_0 X_0 + J_p X_p \geq 0 \tag{32}$$

where the input force X_o is the redox potential of oxidizable substrates, and X_p is the output force representing the phosphate potential, $X_p = -\left[\Delta G_p^0 + RT\ \ln(c_{ATP} / c_{ADP}c_{Pi})\right]$, which drives the ATP utilizing functions in the cell; the ΔG^o 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

$$J_p = L_p X_o + L_{po} X_p \tag{33}$$

$$J_o = L_{op} X_o + L_p X_p \tag{34}$$

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_{op} is the phosphate influence on oxygen flux, while L_{po} shows the substrate dependency of ATP production. Experiments shows that Onsager's reciprocal relations hold for OP, and $L_{op} = L_{po}$.(5)

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 ($\Psi_0 = J_0 X_0$)(4,6)

$$\eta = -\frac{J_p X_p}{J_o X_o} \tag{35}$$

By dividing Eq. (33) by Eq. (34), and by further dividing the numerator and denomerator by $X_0(L_o L_p)^{1/2}$, we obtain the efficiency in terms of the force ratio *x* and the degree coupling q

$$\eta = jx = -\frac{x + q}{q + 1/x} \tag{36}$$

where

$$j = \frac{J_p}{J_o Z},\ x = \frac{X_p Z}{X_o},\ Z = \left(\frac{L_p}{L_o}\right)^{1/2} \text{ and } q = \frac{L_{op}}{(L_o L_p)^{1/2}} \text{ with } 0 < |q| < 1$$

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 η_{opt} is the function of q only, as shown in Figure 3.

$$\eta_{opt} = \left(\frac{q}{1 + \sqrt{1 - q^2}}\right)^2 \tag{37}$$

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_r and the affinity A of reaction ($A = -\sum \nu_i \mu_i$, where the ν_i are the stoichiometic coefficients, which are positive for products and negative for reactants) when $|A| < RT \sim$ 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.(14) 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.(14)

For enzyme-catalyzed and some chemical reactions, under certain boundary conditions, force-flux relationships can be described by a simple hyperbolic-tangent function such as the Michaelis-Menten kinetics, which 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 in between, which extends over an ~7 kJ/mol.(14)

For an elementary chemical reaction the flux J_r is(1)

$$J_r = r_f\left(1 - e^{-A/RT}\right) \tag{38}$$

where the affinity A is expressed in terms of forward r_f and backward r_b reaction rates $A = RT \ln(r_f/r_b)$ as well as in terms of chemical potential. Close to thermodynamic equilibrium, where $A/RT \ll 1$, we can expand Eq. (38) as $J_r = r_{f,eq}(A/RT)$, and compare with the linear reaction flux

$$J_{ri} = -\sum_{i,j} L_{ij} A_j$$

to obtain the phenomenological coefficient as $L_{ij} = r_{f,eq}/(RT)$.

Consider a fluid film having a first order irreversible reaction $B \xrightarrow{k} P$; the evolution equations for heat conduction and diffusion with reaction under nonisothermal conditions are

$$\frac{\partial c_B}{\partial t} = \nabla \cdot \mathbf{J}_B + r_B \tag{39}$$

$$\frac{\partial c_P}{\partial t} = \nabla \cdot \mathbf{J}_p - r_B \tag{40}$$

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot \mathbf{J}_q + (-\Delta H_r) r_B \tag{41}$$

where $r_B = -kc_B$, and c_B and c_P are the concentrations of species of B and P, with the linear phenomenological laws for J_B, J_p, and J_q, Eqs. (39) to (41) become(13)

$$\frac{\partial c_B}{\partial t} = -\nabla \cdot \left(\rho D_{BB} \nabla w_B + \rho D_{BP} \nabla w_P + \rho D_{TB} \nabla \ln T\right) + r_B \tag{42}$$

$$\frac{\partial c_P}{\partial t} = -\nabla \cdot \left(\rho D_{PB} \nabla w_B + \rho D_{PP} \nabla w_P + \rho D_{TP} \nabla \ln T\right) - r_B \tag{43}$$

$$\rho C_p \frac{\partial T}{\partial t} = -\nabla \cdot \left[\rho\left(D_{BB} Q_B^* + D_{PB} Q_P^*\right) \nabla w_B + \rho\left(D_{BP} Q_B^* + D_{PP} Q_P^*\right) \nabla w_P + k \nabla T\right] + (-\Delta H_r) r_B \tag{44}$$

where ΔH_r 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 (ENET)

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.

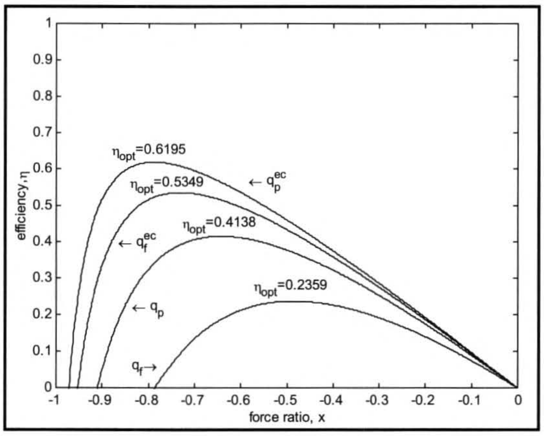

Figure 3. *Change of efficiencies in terms of flux ratios and degree of couplings; for a maximal net rate of ATP flux at optimal efficiency:* $q_f = 0.786$, *for an economic net ATP flux* $(J_p\eta)_{opt}$: $q_f^{ec} = 0.953$, *for a maximal output power* $(J_pX_p)_{opt}$ *at optimal efficiency:* $q_p = 0.910$, *and for an economic net output power* $(J_pX_p\eta)_{opt}$: $q_p^{ec} = 0.972$.[4-6]

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

A	affinity (J mol^{-1})
c	concentration (mol m^{-3}),
D	diffusion coefficient (m^2 s^{-1})
D_T	thermal diffusion coefficient
E	electric potential (V)
F	Faraday constant
F	force per unit mass (kg m s^{-2} kg^{-1})
G	Gibbs' free energy (J)
$\bar{h}$	partial specific enthalpy (J mol^{-1})
h	enthalpy (J)
H_r	heat of reaction (J mol^{-1})
I	current flux
j	ratio of fluxes
J_q	heat flux (J m^{-2} s^{-1})
J_i	mass flux for component *i* (kg m^{-2} s^{-1})
J_r	reaction velocity (flux)
k	thermal conductivity (J $m^{-1}s^{-1}K$), reaction rate constant (s^{-1}),
K_{ij}	phenomenological coefficient (resistance form), Eq. (4)
L_{ij}	phenomenological coefficient (conductance form), Eq. (3)
m	number of fluxes
M	molar mass
n	number of components
N_k	number of moles
P	pressure (Pa)
q	degree of coupling, Eq. (5)
Q*	heat of reaction
r	reaction rate (mol s^{-1})
R	universal gas constant (J $mol^{-1}K^{-1}$)
s	entropy density (J $K^{-1}m^{-3}$)
S	entropy (J $mol^{-1}K^{-1}$)
t	time (s)
T	temperature (K)
u	energy density (J m^{-3})
U	internal energy (J)
v	velocity (m s^{-1})
V	volume (m^3)
$\bar{V}$	partial molar volume (m^3)
w	mass fraction
x	ratio of forces, distance
X	thermodynamic driving force
z	charge (C)
Z	phenomenological stoichiometry

Greek Letters

Φ	entropy production rate (J K^{-1} s^{-1})
Γ	thermodynamic factor
δ	unit tensor
γ	activity coefficient
η	efficiency
μ	chemical potential (J mol^{-1})
ν	stoichiometric coefficients
Π	osmotic pressure (kPa)
ρ	density (kg m^{-3})
τ	viscosity part of stress tensor (kg m^{-1} s^{-2})
ψ	potential energy (J)
Ψ	dissipation function (J s^{-1})

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

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