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Influence of Subenvironmental Conditions and Thermodynamic Coupling on a Simple Reaction-Transport Process in Biochemical Systems

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Supporting Information

ABSTRACT: Living systems must continuously receive substrates from subenvironment, and the population metabolic rate model is affected on this flow of substrates to be metabolized, its relevant variables, and the rate at which operates. This study focuses on the influences of resistances and bulk phase factors with in the subenvironment and by thermodynamic coupling on reaction-transport processes representing a simple enzymatic conversion of a substrate to a product. Thermodynamic coupling refers to mass flow, or a reaction velocity that occurs without or opposite to the direction imposed by its primary thermodynamic driving force. We considered the effects of (i) subenvironment resistances for the heat and mass flows of reacting substrate in the form of the ratios of Sherwood to Nusselt numbers, (ii) the subenvironment bulk phase temperatures and concentration of substrate, and (iii) the cross-coefficients responsible for the induced effects due to the thermodynamic coupling. In order to study these effects, the thermodynamically coupled balance equations using the first order simple elementary reaction are derived and solved numerically. In the balance equations, the linear phenomenological equations are used by assuming that the system is in the vicinity of global equilibrium. The overall results show that the subenvironment factors and cross-coefficients due to thermodynamic coupling may have considerable effects on reaction-transport processes.

1. INTRODUCTION

In order to maintain the self-organization and low-entropy structure processes, living systems must continuously receive nutrients from subenvironment. The population metabolic rate model focuses on this flow of nutrients to be metabolized, its relevant variables, and the rate at which operates.1−14 The metabolism takes place due to the combined effects of many functional, synchronized, and thermodynamically coupled transport and rate processes within the system as a whole. Coupled reaction-transport processes are of great importance in biological systems; many biosynthesis processes, such as synthesis of the complex enzyme macromolecules from the amino acids, are nonspontaneous processes made possible by virtue of being coupled with other spontaneous processes such as oxidation of glucose.14 Thermodynamic coupling refers to heat or mass flow, or a reaction velocity that occurs without or opposite to the direction imposed by its primary thermodynamic driving force as long as the cross-coefficients do not vanish. This is consistent with the statement of the second law, which states that a finite amount of organization may be purchased at the expense of a greater amount of disorganization in a series of coupled processes.6 Some of the coupled processes in living systems include enzymatic reactions, thermal diffusivity in tissues, drug delivery, protein folding, biological oscillations, membrane transport, and the Turing instabilities with appropriate kinetics and large differences in diffusion rates of metabolites.7,15−18

One of the problems in bioenergetics is to understand the ability of complex coupled cycles of metabolism to achieve efficient and functional processes and their adaptation to variable subenvironmental restrictions and topological factors.2−4,8,19 A mathematical model† is used to analyze the transport of electron and proton thermodynamically coupled to adenosine triphosphate (ATP) synthesis in chloroplast by taking into account the nonuniform distribution of electron transport and ATP synthases complexes in the thylakoid of grana and stroma. For example, the rate of electron transfer at the plastoquinone site of the chain could be controlled not only by the intrathylakoid pH but also by the value of pH in the interthylakoid gap, which affects the rate of plastoquinone reduction.3 Also, the rate of ATP synthesis depends on osmotic properties of a chloroplast incubation medium and hence on topological conditions. Turing pattern formation in two-layer coupled reaction-diffusion system is also affected by subenvironment and external influences to transport of substrates. Therefore, bilayer membranes or multilayer tissues under different subenvironments influences could affect the transport processes and hence pattern formation in complex thermodynamically coupled biological systems.5,7

A comprehensive approach toward understanding reaction-transport processes influenced by thermodynamic coupling, and subenvironment factors and resistances would be a valuable tool toward describing and formulating complex biochemical systems. Based on linear nonequilibrium thermodynamics approach,5,6,8,11,19−23 this study presents a thorough analysis

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of thermodynamically coupled balance equations for the reaction-transport processes to illustrate the evolution of mass concentrations and temperatures of the substrate in time and space under the following influences: (i) the subenvironmental resistances to the heat and mass flows of substrates in the form of the ratios of Sherwood number to Nusselt number (Sh/Nu) for a set of bulk phase conditions and cross-coefficients, (ii) the subenvironment bulk phase concentration and temperatures of the substrates for a set of ratios of Sh/Nu and cross-coefficients, (iii) the cross-coefficients for a set of ratios of Sh/Nu and subenvironment bulk phase temperatures and concentrates.

2. REACTION-TRANSPORT PROCESSES WITHOUT THERMODYNAMIC COUPLING

The following simple elementary reaction

\[ \nu g S \xrightleftharpoons[k_i]{k_f} \nu P \]

is considered and may represent simple reaction enzymatic reactions between a substrate and a product, unimolecular isomerization, or racemization of molecules with mirror-image structures with the forward and backward reactions rate constants of \(k_i\) and \(k_f\), respectively.

The well-known balance equations for transport processes with the reaction considered in eq 1 are

\[ \frac{\partial C_S}{\partial t} = -\nabla \cdot \vec{j}_S + \nu g \vec{J}_t \]
\[ \frac{\partial C_P}{\partial t} = -\nabla \cdot \vec{j}_P + \nu P \vec{J}_t \]
\[ \rho \nu g \frac{\partial T}{\partial t} = -\nabla \cdot \vec{q} + \left( \frac{-\Delta H_i}{\beta} \right) \vec{l}_i \]

where \(\Delta H_i\) is the heat of reaction, \(\nu g\) is the stoichiometric coefficient, which is negative for reactants, \(\rho\) and \(\nu P\) are the heat capacity and density, respectively. By using the Fick and Fourier laws in one-dimensional domain of \(y\)-direction, eqs 2 to 4 become

\[ \frac{\partial C_S}{\partial t} = D_S \frac{\partial^2 C_S}{\partial y^2} + \nu g \vec{J}_t \]
\[ \frac{\partial C_P}{\partial t} = D_P \frac{\partial^2 C_P}{\partial y^2} + \nu P \vec{J}_t \]
\[ \rho \nu g \frac{\partial T}{\partial t} = k_e \frac{\partial^2 T}{\partial y^2} + \left( \frac{-\Delta H_i}{\beta} \right) \vec{l}_i \]

where \(D_j\) is the effective diffusivity for species \(i\), and \(k_e\) is the effective thermal conductivity. For simple slab geometry with the half thickness of \(L_j\), the initial and boundary conditions are

\[ t = 0, \quad C_S = C_{S0}, \quad T = T_0 \]
\[ y = \pm L_j, \quad C_S = C_{Sx}, \quad C_P = C_{Px} \]
\[ y = 0, \quad \frac{\partial C_S}{\partial y} = \frac{\partial T}{\partial y} = 0 \quad (\text{symmetry conditions}) \]

where \(C_{Sx}\) and \(C_{Px}\) are the concentrations at the surface of the film. At stationary state, eliminating the reaction terms from eqs 5 and 6, and integrating twice with the boundary conditions given above, concentrations of the species are related to each other by \(\theta_P = a_1 + a_2(1 - \theta_S)\) where \(\theta_P = (C_P / K_{C_P}), \theta_S = (C_S / K_{C_S})\), \(a_1 = (C_P / K_{C_P}), a_2 = (D_{C_P} / K_{C_P})\), and \(K\) is the chemical reaction equilibrium constant. The value of \(a_1\) determines the direction of reaction; the net reaction is toward the \(P\) if \(a_1 < 1\). Also, by eliminating of the reaction terms from eqs 7 and integrating twice with the known boundary conditions, the temperature is related to the concentration by \(\theta = 1 + \beta (1 - \theta)\) where \(\theta = (T / T_s), \beta = ((-\Delta H_P) C_P / (-\nu g) k_e)\). The value of \(\beta\) is a measure of nonisothermal effects; as \(\beta\) approaches zero, the system becomes isothermal.

3. REACTION-TRANSPORT PROCESSES WITH THERMODYNAMIC COUPLING

3.1. Linear Nonequilibrium Thermodynamics. The infinitesimal entropy change \(dS = dS_{\text{sub}} + dS_{\text{reaction}}\) consists of the entropy flow \(dS_{\text{sub}} = -dS_{\text{transport}}\) into the system from the subenvironment and the internal rate of local entropy production \(dS_{\text{reaction}}\). The total local rate of entropy production is expressed by \(dS_{\text{reaction}} / dt = J_{iS} / \Delta S_{iS}\) where \(J_i\) and \(X_i\) are the conjugate flows and forces, respectively. Linear phenomenological equations relate the flows to the forces \(J_i = \Sigma L_{ik} X_k\) where the \(L_{ik}\) represent the primary \(i = k\) and the cross-coefficients \(i \neq k\). These coefficients satisfy the various constraints, such as Onsager’s reciprocity, Gibbs–Duhem equation at equilibrium, and the choice of reference frame for diffusivities. A necessary and sufficient condition for \(dS_{\text{reaction}} / dt \geq 0\) is that all its principal minors of the coefficients matrix \([L]\) be non-negative \(L_{ij} > 0\) \(i = 1,2 \ldots n\) and \(L_{ik} > (1/4)(L_{ik} + L_{ki})^2\) \(i \neq k\). Some of the coefficients \(L_{ik}\) may be identified using Fick’s, Fourier’s, and the mass action laws.

The reaction velocity \(J_i\) is mostly expressed as \(J_i = J_{i0} (1 - \exp(-A/RT))\). If we expand this equation and consider the near global equilibrium state where the Gibbs free energy is less than 1.5 kJ/mol or \(A / RT < 1\), then we may assume a linear relationship between the reaction velocity and the chemical affinity for an elementary reaction \(J_i = J_i = J_{i0} A / T = J_{i0} \exp(A / (RT))\) where \(L_{ik} = J_{i0} \exp(A / (RT))\) and depends on the rate constant and consequently on the equilibrium concentration \(C_{i0}\) and the amount of chemical catalyst. Some biological pathways occur at near global equilibrium conditions. By the conservation of mass, some flow-force relations of the enzyme catalyzed and other chemical reactions can be described by a simple hyperbolic-tangent function.

The rate of entropy production for a simple one-dimensional heat conduction is \(dS_{\text{reaction}} / dt = -dJ_{q} / (dT / dx) > 0\), where \(J_q = -L_{q0} (d^2 T / dx^2)\), which is identical to Fourier’s law of heat conduction with \(k = L_{q0} / T^2\). The equation for \(J_q\) is valid when the relative variation of temperature is small within the mean free path distance \(\lambda\) in the case of gases (\(\lambda / T \ll \langle d T / d x \rangle \) \(\ll 1\). Since this condition is satisfied for most systems, the linear phenomenological equations are satisfactory approximations for...
transport processes. The LNET formulation does not require the mechanism of the thermodynamic coupling.

### 3.2. Local Rate of Entropy Production

Local rate of entropy production for reaction-transport processes is given by

\[
\frac{dS}{dt} = J_L \cdot V \left( \frac{1}{T} - J_L \frac{\langle V \mu \rangle_{r,F}}{T} - J_r \frac{\langle V \mu \rangle_{r,F}}{T} \right) + J_{Sp} A \geq 0
\]

(9)

where \( \langle V \mu \rangle_{r,F} \) is the partial molar volume of species \( i \). Equation 10 becomes

\[
\frac{dS}{dt} = -J_L \left( \frac{1}{T} \right) VT - J_s \frac{1}{T} \delta_s V C_s + J_{Sp} A \geq 0
\]

(10)

where \( J_L = \left(1 + (C_i/C_p) \right) \frac{\partial \mu_i}{\partial C_i} \left|_{T,P} \right. \) for \( V_s \approx V_p \), \( J_L \) is the molar flow of species \( i \), \( \mu_i \) is the chemical potential of species \( i \), \( A \) is the affinity (\( A = -\sum_\mu \mu_i \)), \( J_t \) is the reaction velocity (rate) \( \left( \frac{df}{dt} \right) = \left( \frac{dc}{dt} \right) \), and \( J_s \) is the vector of reduced heat flow \( J_s = q - \sum_\mu \mu_i J_t \), where \( q \) is the total heat flow, \( h_i \) is the partial molar enthalpy of species \( i \). Equation 10, excludes pressure, viscous, electrical, and magnetic effects; it consists of scalar processes of chemical reactions and vectorial processes of heat and mass flows.

### 3.3. Linear Phenomenological Equations

Equation 10 identifies the independent conjugate flows \( J_i \) and forces \( X_i \) to be used in the following linear phenomenological equations when the system is in the vicinity of global equilibrium.

\[
J_S = -L_{SS} \frac{1}{T} \delta_S V C_S - L_{SQ} \left( \frac{1}{T^2} \right) VT + L_{Sp} A \frac{1}{T}
\]

(11)

\[
J_q = -L_{qS} \frac{1}{T} \delta_S V C_S - L_{qQ} \left( \frac{1}{T^2} \right) VT + L_{qP} A \frac{1}{T}
\]

(12)

\[
J_r = -L_{rS} \frac{1}{T} \delta_S V C_S - L_{rQ} \left( \frac{1}{T^2} \right) VT + L_{rP} A \frac{1}{T}
\]

(13)

Equations 11 to 13 represent the thermodynamically coupled reaction-transport processes where the flows are the function of all the forces present within the system. The coefficient matrix \([L]\) is symmetric and its elements obey the Onsager rule \( L_{ij} = L_{ji} \). Equations 11 to 13 introduce cross-coefficients between heat and mass flows \( L_{iQ} = L_{Qi} \) heat flow and chemical reaction velocity \( L_{iq} = L_{qI} \), and mass flows and chemical reaction velocity \( L_{qS} = L_{Sq} \). These cross-coefficients can be related to the kinetic parameters and transport coefficients, and control the induced effects because of the thermodynamic coupling.

The Curie–Pruigne principle states that “quantities whose tensorial characters differ by an odd number of ranks cannot interact in an isotropic medium.” Since the flows (fluxes) should have the same symmetry elements (symmetric under arbitrary space rotations and under space parities), a scalar flow, such as the rate of reaction, cannot be coupled with a vectorial flow of a transport process in an isotropic medium where an equilibrium-dividing surface is symmetric with respect to rotations around any local normal vector. However, the symmetry properties alone are not sufficient for identifying physical coupling; the actual physics considered in deriving the entropy production equation and the specific structure, such as anisotropy, are necessary. Thus, in asymmetric membrane diffusion flows cannot be directly coupled to chemical reactions taking place in the membrane. However, in asymmetric membrane such coupling may be possible.

### 3.4. Phenomenological Coefficients

Some processes will not be dependent on some of the forces when the appropriate cross-coefficients naturally vanish. For example, some degrees of imperfections do to parallel pathways of reaction or intrinsic uncoupling within the pathway itself may lead to leaks and slips in mitochondria. This, however, may add complexity to the phenomenological analysis, because failure of models to fit the properties of a system may be the result of, for example, unaccounted coupling.

The diagonal elements of the phenomenological coefficients matrix \([L]\) may be identified using the Fick, Fourier, and the mass action laws. Comparison of the first term on the rhs of eq 11 with Fick’s law \( (J = -D_{sq} V C_S) \) yields \( L_{SS} = D_{sq} T/\lambda_s \). Similarly, comparison of the second term on the rhs of eq 12 with Fourier’s law \( (J_q = -k_q VT) \) yields \( L_{qQ} = k_q T^2 \). The cross-coefficients \( L_{SQ} \) may be represented by the Soret coefficient \( \lambda_{sf} \) that is related to the thermal diffusion and the Dufour effect, respectively \( D_{sf} = L_{SS} (1/T^2) = r_T L_{Sf} C_S = D_{sf} C_S \) and \( D_{qf} = L_{qQ} (1/T) = k_q L_{qf} C_S \). With these newly defined primary \( L_{sf} \) and cross-coefficients \( L_{qf} \), eqs 11 to 13 become

\[
J_S = -D_{sq} V C_S - D_{sf} T \frac{1}{T} VT + L_{Sp} A \frac{1}{T}
\]

(14)

\[
J_q = -D_{qf} A V C_S - k_q VT + L_{qP} A \frac{1}{T}
\]

(15)

\[
J_r = -L_{rS} \left( \frac{1}{T^2} \right) VT - L_{rQ} \left( \frac{1}{T^2} \right) VT + \frac{k_q C_{qf}}{R} A \frac{1}{T}
\]

(16)

When we can control the temperature and concentration gradients, the coupling coefficients between the chemical reaction and the flows of mass and heat may be determined experimentally. For a closed system at stationary state \( J_S = 0 \), and using \( A = RT \ln(J_r/J_S) \) in eq 14, we get

\[
L_{SQ} = \frac{1}{R \ln(J_r/J_S)} \left( D_{SF} V C_S + D_{qf} VT \right) = L_{qf}
\]

(17)

On the other hand, at chemical equilibrium, where \( A = 0 \) and \( J_r = 0 \), we have

\[
J_r = 0 = -L_{rS} \left( \frac{1}{T^2} \right) VT - L_{rQ} \left( \frac{1}{T^2} \right) VT
\]

(18)

and the two coupling coefficients are related to each other \( L_{qf} = -L_{rS} T \left( V C_S/VT \right) = L_{qf} \). By using the relationship \( -C_{sf}T = V C_S/VT \) at steady state, the coefficient \( L_{qf} \) in terms of the Soret coefficient \( \lambda_{sf} \) becomes \( L_{qf} = L_{rS} T \lambda_{sf} C_S T / \lambda_T \), and we get

\[
L_{SQ} = \frac{T \lambda_{sf} C_S T}{(A/T)} \left[ D_{sq} V C_S + D_{sf} T VT \right] = L_{qf}
\]

(19)

Equations 17 and 19 suggest that the cross-coefficients \( L_{qf} \) and \( L_{rS} \) are related to the gradients of concentration and temperature, and control the induced effects between vectorial flows of heat and mass, and the scalar reaction velocity in an anisotropic medium.

The coefficients help determine the degree of coupling between a pair of flows; the degree of coupling between the unidirectional heat and mass flows \( q_{Sqf} \) and between the...
chemical reaction and the unidirectional heat and mass flows, \( q_{\text{h}} \) and \( q_{\text{q}} \) are\(^{5,19,28} \)

\[
q_{\text{h}} = \frac{L_{\text{eq}}}{(L_{\text{eq}}L_{\text{h}})^{1/2}}, \quad q_{\text{q}} = \frac{L_{\text{q}}}{(L_{\text{q}}L_{\text{eq}})^{1/2}},
\]

(20)

### 3.5. Thermodynamically Coupled Balance Equations.

By inserting eqs 14 to 16 into eq 4 and eq 6, we may describe the thermodynamically coupled system of chemical reaction and the flows of heat and mass by

\[
\frac{\partial C_s}{\partial t} = -\left[V \left( -D_{\text{ce}} V C_s - D_{\text{re}} VT + L_{\text{eq}} \frac{A}{T} \right) \right] - \left( -L_{\text{eq}} \frac{\lambda_s}{T} V C_s - \frac{L_{\text{eq}}}{T^2} \frac{\lambda_s}{T} VT + \frac{k_i C_{\text{eq}}}{R} \frac{A}{T} \right)
\]

(21)

\[
\rho c_p \frac{\partial T}{\partial t} = -V \left( -D_{\text{ce}} V C_s - k_i VT + L_{\text{eq}} \frac{A}{T} \right) + (-\Delta H_i) \left( -L_{\text{eq}} \frac{\lambda_s}{T} V C_s - \frac{L_{\text{eq}}}{T^2} \frac{\lambda_s}{T} VT + \frac{k_i C_{\text{eq}}}{R} \frac{A}{T} \right)
\]

(22)

Under mechanical equilibrium, we have

\[
\nabla \left( \frac{\mu}{T} \right) = -H_i \frac{VT}{T^2} + \frac{\left( V \mu \right) T}{T}
\]

(23)

where \( H_i \) is the partial enthalpy of species \( i \). By using the definition of affinity (\( A = \mu_s - \mu_p \)), the Gibbs–Duhem equation \( (C_s \nabla \mu_s + C_p \nabla \mu_p = 0) \), \( \lambda_s = (1 + (C_s/C_p)) (\partial \mu_s/\partial C_{eq}) \), we obtain

\[
\nabla \left( \frac{A}{T} \right) = \nabla \left( \frac{\mu}{T} \right) - \frac{\lambda_s}{T} V C_s - \frac{(-\Delta H_i)}{T^2} VT
\]

(24)

Substituting eq 24 in eq 21 and 22, we have

\[
\frac{\partial C_s}{\partial t} = D_{\text{ce}} V^2 C_s + D_{\text{re}} V^2 T + \left( -L_{\text{eq}} \frac{\lambda_s}{T} V C_s - \frac{L_{\text{eq}}}{T^2} \frac{\lambda_s}{T} VT + \frac{k_i C_{\text{eq}}}{R} \frac{A}{T} \right) VT - I
\]

(25)

\[
\rho c_p \frac{\partial T}{\partial t} = D_{\text{ce}} V^2 C_s + k_i V^2 T - \left( \frac{\lambda_s}{T} \right) \left( \frac{(-\Delta H_i) L_{\text{eq}} + L_{\text{eq}}}{T} \right) I
\]

(26)

where

\[
I = \left[ C_{\text{eq}} k_o \exp \left( -\frac{E_i}{RT} \right) \left( E_b - E_i \right) \frac{E_b}{RT} + \ln \frac{C_s}{C_p} \right]
\]

(27)

where \( b = L_{\text{eq}} + L_{\text{eq}} (-\Delta H_i) = ((k_C C_{\text{eq}}) T)/(k_T T q^2 + (D_{\text{eq}}/\lambda_s)) \)

and

\[
A^s = \left( \frac{E_b - E_i}{T} + \frac{\theta_s}{\lambda_s} \right) + \ln \left( \frac{T_{\text{eq}}}{k^2} \left( a_1 + a_2 (1 - \theta_s) \right) \right)
\]

(28)

where \( D_{\text{eq}} \) is the Damkohler number for component \( i \), and measures the intrinsic rates of the reaction relative to that of the diffusion.

Equations 30 and 31 suggest that the induced effects due to the coupling phenomena and subenvironmental effects can increase the possibility that the system may evolve to multiple
states and diversify its behavior. The parameters $\varepsilon$, $\sigma$, $\omega$, and $\kappa$ above are associated with the cross-coefficients and hence control the coupled phenomena in the $y$-direction. Specifically, the $\varepsilon$ and $\omega$ control the coupling between mass and heat flows, while the $\sigma$ and $\kappa$ control the coupling between the chemical reaction and mass flow, and chemical reaction and heat flow, respectively.

The nondimensional forms of initial and boundary conditions described in eq 29 become

\[
\begin{align*}
\tau &= 0, \quad \theta_s = \theta_{sh}, \quad \phi = \phi_s \\
z &= \pm 1, \quad r > 0, \quad \frac{\partial \theta}{\partial z} = S_b(\theta_{sh} - 1), \quad \frac{\partial \phi}{\partial z} = \text{Nu} \ (\phi_b - 1) \\
z &= 0, \quad r > 0, \quad \frac{\partial \theta}{\partial z} = \frac{\partial \phi}{\partial z} = 0
\end{align*}
\]

where the $\text{Sh}$ and $\text{Nu}$ are the Sherwood and Nusselt numbers, $\text{Sh}/\text{Nu} = (k_LD_b)/(hL/k_c)$ respectively. The dimensionless subenvironmental bulk phase concentrations of $S$ is denoted by $\theta_{sh}$ and whereas $\phi_b$ is the dimensionless subenvironmental bulk phase temperature. Accuracy of the solutions obtained from eqs 30 and 31 depends on the reliable data, such as the effective transport coefficients and cross-coefficients. Some processes will not be dependent on some of the forces when some of the cross-coefficients vanish naturally. For example, some degrees of imperfections due to parallel pathways of reaction or intrinsic uncoupling within the pathway itself may lead to leaks and slips in mitochondria.

The balance equations of $S$ and $\phi$ can be combined at steady state as follows

\[
\frac{d^2}{dy^2} \left( D_C C_S + \frac{k_T}{\text{-} \Delta H_T} \right) = 0
\]

and integrated twice from the center to the surface using the boundary conditions addressing the subenvironmental conditions given in eq 29. The integration yields the following sum of external and internal temperature differences

\[
T - T_b = (- \Delta H_T) \frac{k_S}{h} (C_b - C_{sh}) + (- \Delta H_T) \frac{D_C}{k_c} (C_{sh} - C_b)
\]

The maximum temperature difference occurs when all the substrate is consumed ($C_s = 0$), and after rearranging the terms, the effect of the ratio ($\text{Sh}/\text{Nu}$) on the subenvironmental conditions are obtained

\[
\frac{(T - T_b)_{\text{max}}}{T_b} = \beta \frac{\text{Sh}}{\text{Nu}} \left( 1 - \frac{C_{sh}}{C_b} \right) + \frac{C_{sh}}{C_b}
\]

### 4. RESULTS AND DISCUSSION

Nondimensional forms of eqs 30–31 representing the one-dimensional thermodynamically coupled reaction-transport processes are solved numerically using MATLAB with initial and boundary conditions given in eq 32 to determine the changes of $\theta_b$ and $\phi$ in space and time. To illustrate the subenvironmental influences and of the thermodynamic coupling on the reaction-transport systems, we considered the following:

(i) Subenvironment resistances to the heat and mass flows of the substrates in the form of the ratios of Sherwood to Nusselt numbers ($\text{Sh}/\text{Nu}$) for a set of subenvironment bulk phase conditions and cross-coefficients shown in Table 1.

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<td>n.u.</td>
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<td>n.u.</td>
</tr>
<tr>
<td>$(\sigma)_L$</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>$(\sigma)_H$</td>
<td>n.u.</td>
<td>n.u.</td>
<td>n.u.</td>
</tr>
<tr>
<td>$(\kappa)_L$</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>$(\kappa)_H$</td>
<td>n.u.</td>
<td>n.u.</td>
<td>n.u.</td>
</tr>
</tbody>
</table>

*Boldface parameters are used for comparison, while keeping other parameters constant. n.u.: not used. L: lower value. H: higher value.

(ii) Subenvironment bulk phase concentration and temperature of the substrates for a set of the ratios of $\text{Sh}/\text{Nu}$ and cross-coefficients shown in Table 1.

(iii) Cross-coefficients for a set of the ratios of $\text{Sh}/\text{Nu}$ and subenvironment bulk phase conditions for substrates, as shown in Table 1.

The values of parameters and coefficients used in this study are in line with the previously established limits. The solutions are for slow chemical first order reactions ($D_{S\phi} = 0.01$). The nondimensional group $\beta$ (thermicity), which is the ratio of heat generation due to the reaction and rate of heat conduction, is kept constant at a value of 0.1. The Arrhenius $(\gamma)$ and Lewis numbers $(Le)$ are kept constant during the study.

### 4.1. Influences of Subenvironment Resistances to Heat and Mass Flows

The ratio of $\text{Sh}/\text{Nu}$ is largely dependent on the rates of heat and mass flows in subenvironment, and may be one of the controlling parameters for mass and/or heat transfer limited chemical systems, such as DNA–protein and DNA–RNA interactions. The considered low and high values for the ratio of $\text{Sh}/\text{Nu}$ are 0.1 and 20, respectively, to represent the effects of subenvironment resistances to heat and mass flows (see Table 1 for the values of other parameters). Figure 1 displays the surface plots of changes for $\theta_b$ and $\phi$ with time and space at high and low ratios of $\text{Sh}/\text{Nu}$. Supporting Information Figure S1 shows the two-dimensional plots representing the effects of subenvironment resistances to the heat and mass flows of the substrates in the form of the ratios of Sherwood to Nusselt numbers ($\text{Sh}/\text{Nu}$) with space ($\tau = 1$) and time ($z = 1$) for a set of subenvironment bulk phase conditions and cross-coefficients shown in Table S1, Supporting Information. The ratio $\text{Sh}/\text{Nu}$ of 20 shows greater end effects on the surface of $\theta_b$ than the
Effects due to Sh/Nu of 0.1 (Figure 1a and c). When the ratio Sh/Nu = 20, the $\theta_S$ decreases considerably while $\phi$ increases only slightly in both time and space, indicating little resistance for the mass flow from bulk to the surface and eventually to the reacting site (Figure 1c). On the other hand, if the ratio is less than one (Sh/Nu = 0.1), the heat flow is faster and lower rate of mass flows lead to the small decrease in $\theta_S$ while considerable increase in $\phi$ in both time and space (Figure 1a). The end effects are also noticeable in Figure 1b, where $\phi$ increases to 1.0025, while at Sh/Nu = 0.1 $\phi$ increases to 1.0006 (Figure 1d).

Figure 1. Surface plots showing the changes in $\theta_S$ and $\phi$ for coupled reaction-transport system with subenvironmental resistance in time and space keeping other parameters constant listed in Table 1: (a and b) Sh/Nu = 0.1; (c and d) Sh/Nu = 20.

Figure 2. Surface plots showing changes $\theta_S$ and $\phi$ with subenvironmental bulk substrate concentration and temperature in time and space keeping other parameters constant listed in Table 1: (a and b) $\theta_{Sb} < 1$, $\phi_{b} < 1$; (c and d) $\theta_{Sb} > 1$, $\phi_{b} > 1$. 
As Figure 1, parts b and d, shows, temperature changes are quite visible at when Nu > Sh. Figure 1d indicates a sharp change of temperature toward the end of space region of around z = 0.7. Therefore, if the mass flow is slower, such as reactants in a gaseous phase and the enzyme is in the solid phase, the heat flow becomes an important factor to the overall reaction.

4.2. Influences of Subenvironment Bulk Phase Conditions. The bulk concentration and bulk temperature can affect various biochemical events and biological processes. For example, the nitrogen source concentration (bulk concentration) can influence the microalgal growth and neutral lipid production. The bulk temperature also impacts transport processes and protein folding within the cell. The dimensionless values of bulk concentrations and bulk temperature considered are \( \theta_{sb} < 1 \) and \( \phi_{b} < 1 \) and \( \theta_{sb} > 1 \) and \( \phi_{b} > 1 \) (with other parameters listed in Table 1). Figure 2 shows surface plots of concentration and temperature illustrating an inverse behavior for the values of bulk concentration as well as temperature for higher and lower values than one. Supporting Information Figure S2 shows two-dimensional plots indicating the effects of subenvironment bulk phase concentration and bulk temperatures on \( \theta_{b} \) and \( \phi \) with space \( (r = 1) \) and time \( (z = 1) \) for a set of the ratios of Sh/Nu and cross-coefficients shown in Table S1, Supporting Information. The substrate concentration consistently decreases with \( \theta_{sb} < 1 \) and \( \phi_{b} < 1 \) (Figure 2a) and increase uniformly with \( \theta_{sb} > 1 \) and \( \phi_{b} > 1 \) (Figure 2c). When \( \theta_{sb} > 1 \) and \( \phi_{b} > 1 \), the change in substrate concentration remains almost constant with the value around 1.00–1.10 with space at \( r = 1 \), and 1.00–1.05 with time at \( z = 1 \). On other hand, when, the substrate concentration decreases rapidly from 1.00 to 0.30, and from 0.60 to 0.30 with \( r \) at \( z = 1 \). It is evident from the temperature profiles (Figure 2b and d) that the changes in temperature are mostly at \( z \geq 0.7 \). Therefore, a slight increase in temperature can be observed for \( \theta_{sb} > 1 \) and \( \phi_{b} > 1 \), and the decrease is quite rapid when \( \theta_{sb} < 1 \) and \( \phi_{b} < 1 \), toward the end of space around \( z \geq 0.7 \) can be detected. Consequently, in order to attain effective substrate conversion and temperature utilization, the bulk resistances must be low. Hence, impact of subenvironment bulk condition is one of the important factors that control the changes of concentration and temperature in reaction-transport processes.

4.3. Influence of Thermodynamic Coupling. Equations 30 and 31 are for thermodynamically coupled system of unidirectional reaction-transport processes with some unique cross-coefficients between the chemical reaction and heat and mass flow, and between mass and heat flows. The cross-coefficient \( \sigma \) controls the coupling between the chemical reaction velocity and heat and mass flow, \( \kappa \) controls the coupling between the chemical reaction velocity and heat flow, \( \epsilon \) controls the coupling between heat and mass flows involving Dufour effect on the thermodynamically coupled reaction-transport systems. The solutions shown in Figure 3 are for low values (0.0001) and high values (0.9) for the cross-coefficients of \( \sigma, \kappa, \epsilon, \) and \( \omega \), while keeping the same subenvironment resistances and bulk conditions as shown in Table 1. Supporting Information Figure S3 shows two-dimensional plots summarizing the effects of cross-coefficients involved in coupling of reaction-heat flow, reaction-mass flow, and heat-mass flows on \( \theta_{b} \) and \( \phi \) with space \( (r = 1) \) and time \( (z = 1) \) for a set of the ratios of Sh/Nu, and bulk substrate concentration and temperature shown in Table S1, Supporting Information. The overall effects of thermodynamic coupling on substrate profile can be observed in the surface plots, where the conversion is relatively greater for high values of cross-coefficients (Figure 3). For both high and low values of the cross-coefficients, \( \theta_{b} \) reduces with time and space. The
respectively. The conversion rate and distribution analysis of \( \theta \) for high and low values of \( \omega \) is shown in Figure 3a and c. The major effects of the cross-coefficients representing reaction-heat flow\( (\kappa)\), reaction-mass flow\( (\sigma)\), and heat-mass flows\( (\epsilon\) and \(\omega)\) can be observed in the temperature profile in time and space, as shown in Figure 3b and d. The high values of cross-coefficients result in rapid changes in temperature with time, whereas, in space, the temperature values remain constant until \( z \leq 0.9 \), and then rapidly increased until \( z = 1 \). The value of \( \phi \) increases from 1.00 to 1.12 with time for \( z = 1 \) for high values of cross-coefficients, whereas remains almost constant for low values. The distribution of \( \phi \) with space \((\tau = 1)\) shows a shift from 1.00 to 1.10 at \( z = 0.9 \) to 1.0 for higher values of cross-coefficients, whereas the lower values, as similar to change in \( \phi \) with time, have a little change with space. Therefore, the change in \( \phi \) with both space and time increases significantly for high values of cross-coefficients \((\sigma = \kappa = \epsilon = \omega = 0.9)\) lower than lower values \((\sigma = \kappa = \epsilon = \omega = 0.0001)\). This indicates that the cross-coefficients play a significant role in terms of utilization of substrate and controlling temperature and hence, thermodynamic coupling could provide an insight in understanding reaction-transport processes in chemical and biochemical systems, such as the primary active transport, which requires the energy released by the hydrolysis of adenosine triphosphate in biological cells.5,12,27,28

4.4. Biological Significance of Thermodynamic Coupling. In order to characterize any biological system, the initial and boundary conditions considering subenvironmental resistances are imposed along with concentration of substrates and temperature. The effects of subenvironmental resistances, bulk phase conditions, and cross-coefficients could easily influence the efficiency of coupling.6 Table 2 represents the related parameters used in this study with their respective definition and significance. These parameters have physical and biological meaning to the thermodynamically coupled reaction-transport processes. 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. Turing represents the reaction-diffusion systems with appropriate nonlinear kinetics in a homogeneous steady state generating stable patterns.7 The complexity of biochemical network systems is due to multiple interconnected branches and cycles, involving a number of coupled enzymatic processes. These enzymes sequentially convert different substrate with feedback and feed forward loop. For instance, primary active transport in biological cells involves hydrolysis of ATP coupled with the flows of sodium ions outside of the cell. In this case, ATP synthesis is matched and synchronized to cellular ATP utilization for the level of trans-membrane proton transport as well as other transport systems such as primary active transport of sodium–potassium pumps as shown in Figure 4. As a result, the hydrolysis of ATP is coupled to transporting protons, and maintaining the thermodynamic force of electrochemical ion gradients.9,12,14,23,26–28,31 Consequently, these cross-coefficients

![Figure 4. Primary active transport for Na⁺ and K⁺ pumps representing the thermodynamically coupled reaction-transport processes.](Image 372x91 to 517x229)
may also be useful in understanding of protein folding, biological oscillations, membrane transport, and various coupled biological phenomena. Modeling of biological systems requires quantitative predications of the coupling and subenvironmental conditions representing the metabolic reaction-transport processes.

The energy level of a reactant may change due to the coupling effect, while the catalyst effect may be limited to the lowering of the reaction barrier for both the forward and backward reactions. Many biological reactions can take place against their own affinities because of the thermodynamic coupling effect. For example, many transport systems in bacteria are driven by the proton gradient across the plasma membrane. At the same time, protons are transported out of the cell in connection with electron flow through the respiratory chain. Overall, the cell maintains a nonequilibrium level of pH by keeping its interior at a higher pH than its environment. Eukaryotic cells possess a hierarchy of transport systems to maintain nonequilibrium concentration levels of some substrates within organelles than those in the cell’s cytoplasm. Still, the cell controls its complex array of chemical systems to maintain nonequilibrium concentration levels of some substrates within organelles than those in the cell’s cytoplasm.

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4.5. Special Reaction-Transport Cases. When there is no coupling between the flow of hydrogen and ATP production, we have \( K_{\text{H}} = K_{\text{Hf}} = 0 \); using eqs 38 and 39 the phenomenological equations become

\[
\eta = -\frac{J_p X_p}{J_A}
\]  

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\[
\eta = -\frac{J_p X_p}{J_A}
\]  

Uncoupling proteins are a subgroup of the mitochondrial anion transporter family, and are identified in prokaryotes, plants, and animal cells. The uncoupling of the mitochondrial electron transport chain from the phosphorylation of ADP is physiological, optimizes the efficiency, and fine-tunes the degree of coupling of oxidative phosphorylation. When we have level flow, the force vanishes, \( \Delta \tilde{\mu}_j = 0 \), and eqs 38 to 40 reduce to

\[
A_p^{\text{ex}} = K_p J_p + K_{\text{PO}} J_O
\]  

\[
A_{\text{H}}^{\text{ex}} = K_{\text{H}} J_{\text{H}} + K_{\text{OH}} J_O
\]  

\[
A_O^{\text{ex}} = K_{\text{OH}} J_{\text{H}} + K_{\text{O}_2} J_O
\]  

and the effective degree of coupling becomes

\[
q = \frac{q_{\text{PO}} + q_{\text{OH}} J_O}{(1 - q_{\text{PO}}^2)(1 - q_{\text{OH}}^2)}
\]  

Using eqs 30–32, four cases of reaction-transport systems are analyzed.

Case i. No coupling between the flows of heat and mass involving Soret effect: \( \varepsilon = 0 \); the modeling equations become

\[
\frac{\partial \delta_S}{\partial \tau} = \frac{\partial^2 \delta_S}{\partial z^2} + \frac{\sigma}{\phi^2} \frac{\partial \phi}{\partial z} - A^*\text{Da}\delta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

\[
\frac{1}{L_e} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} + \frac{\omega}{\phi^2} \frac{\partial \phi}{\partial z} - \frac{\kappa}{\phi} \frac{\partial \delta_S}{\partial z} + A^*\text{Da}\theta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

Equations 47, 48, and 32 are solved with respective parameters given in Table 1, and simulations are summarized in Figure S4 within the Supporting Information.

Case ii. No coupling between heat and mass flows involving Dufour effect: \( \omega = 0 \); the modeling equations become

\[
\frac{\partial \delta_S}{\partial \tau} = \frac{\partial^2 \delta_S}{\partial z^2} + \frac{\epsilon}{\phi^2} \frac{\partial \phi}{\partial z} - A^*\text{Da}\delta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

\[
\frac{1}{L_e} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} - \frac{\kappa}{\phi} \frac{\partial \delta_S}{\partial z} + A^*\text{Da}\theta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

Equations 49, 50, and 32 are solved with respective parameters given in Table 1, and simulations are summarized in Figure S5 within the Supporting Information.

Case iii. No coupling between the chemical reaction velocity and mass flow: \( \sigma = 0 \); the modeling equations become

\[
\frac{\partial \delta_S}{\partial \tau} = \frac{\partial^2 \delta_S}{\partial z^2} + \frac{\epsilon}{\phi^2} \frac{\partial \phi}{\partial z} - A^*\text{Da}\delta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

\[
\frac{1}{L_e} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} - \frac{\kappa}{\phi} \frac{\partial \delta_S}{\partial z} + A^*\text{Da}\theta \theta_{\text{Seq}} \exp \left[ \gamma \left( 1 - \frac{1}{\phi} \right) \right]
\]  

Equations 49, 50, and 32 are solved with respective parameters given in Table 1, and simulations are summarized in Figure S5 within the Supporting Information.
\[ \frac{\partial \theta_s}{\partial \tau} = \frac{\partial^2 \theta_s}{\partial z^2} + \epsilon \frac{\partial^2 \phi}{\partial z^2} - A^* \text{Da} \theta_{S\text{eq}} \exp \left( \gamma \left( 1 - \frac{1}{\phi} \right) \right) \] (51)

\[ \frac{1}{\text{Le}} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} + \omega \frac{\partial \theta_s}{\partial z} + A^* \text{Da} \beta \theta_{S\text{eq}} \times \exp \left( \gamma \left( 1 - \frac{1}{\phi} \right) \right) \] (52)

Equations 51, 52, and 32 are solved with respective parameters in Table 1, and simulations are summarized in Figure S6 within the Supporting Information.

Case iv. No coupling between the chemical reaction velocity and heat flow: \( \kappa = 0 \); the modeling equations become

\[ \frac{\partial \theta_s}{\partial \tau} = \frac{\partial^2 \theta_s}{\partial z^2} + \epsilon \frac{\partial^2 \phi}{\partial z^2} + \sigma \frac{\partial \phi}{\partial z} - A^* \text{Da} \theta_{S\text{eq}} \times \exp \left( \gamma \left( 1 - \frac{1}{\phi} \right) \right) \] (53)

\[ \frac{1}{\text{Le}} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} + \omega \frac{\partial \theta_s}{\partial z} + A^* \text{Da} \beta \theta_{S\text{eq}} \times \exp \left( \gamma \left( 1 - \frac{1}{\phi} \right) \right) \] (54)

Equations 53, 54, and 32 are solved with respective parameters in Table 1, and simulations are summarized in Figure S7 within the Supporting Information.

5. CONCLUSIONS

The modeling equations developed in the dimensionless and unidirectional forms are solved for a systematic study of the influences of external and internal factors on reaction-transport processes in space and time for an enzymatic conversion of a substrate to a product within the metabolic cycle. The external factors considered are the influences of subenvironmental resistances to mass and heat flows as well as the bulk phase conditions, while the internal factors are the induced effects controlled by the unique cross-coefficients because of thermodynamic coupling between transport processes and enzymatic reaction. The representative solutions display the effect of each influence on the substrate concentration and temperature in both time and space when the other possible influences are kept the same. However, the complex coupled biochemical cycles will be affected by all types of these influences simultaneously. Yet, the comprehensive modeling presented in this study may provide a thorough analysis tool for understanding the effects of subenvironmental conditions and induced effects because of thermodynamic coupling on the reaction-transport processes in chemical and biochemical systems when they are in the vicinity of equilibrium.

ASSOCIATED CONTENT

Supporting Information
SA: Two-dimensional plots for changes in \( \theta_s \) and \( \phi \) with space (at \( \tau = 1 \)) and time (at \( z = 1 \)) using the parameters in Table S1 are given in Figures S1, S2, and S3. SB: Special reaction transport cases: (i) no coupling between the flows of heat and mass involving Soret effect (Figure S4), (ii) no coupling between heat and mass flows involving Dufour effect (Figure S5), (iii) no coupling between the chemical reaction velocity and mass flow (Figure S6), and (iv) no coupling between the chemical reaction velocity and heat flow (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

NOMENCLATURE

\( A \) chemical affinity, J/mol
\( \text{Da} \) Damköhler number
\( D_s \) effective diffusion coefficient for the substrate \( S \), m\(^2\)/s
\( D_{\text{D}} \) coupling coefficient related to the Dufour effect, J m\(^2\)/mol s
\( D_{\text{E}} \) coupling coefficient related to the thermal diffusion (Soret) effect, mol/(m s K)
\( E \) activation energy of the chemical reaction, J/mol
\( \Delta H_r \) reaction enthalpy J/kg
\( h \) heat transfer coefficient, J/(m\(^2\) K)
\( H_i \) partial enthalpy, J/kg
\( J \) diffusive molar flux, mol/(m\(^2\) s)
\( J_a \) conduction heat flux, W/m\(^2\)
\( J_r \) volumetric reaction rate, mol/(m\(^3\) s)
\( k \) effective thermal conductivity, W/(m K)
\( \text{Le} \) Lewis number
\( L_{ak} \) phenomenological coefficients
\( L_{aq} \) element of coupling coefficient between chemical reaction and heat flow, mol K/(m\(^2\) s)
\( L_a \) element of coupling coefficient between chemical reaction and mass flow of component \( i \), mol\(^2\) K/(J m\(^2\) s)
\( \text{Nu} \) Nusselt number (\( \text{Nu} = hL/k \))
\( R \) gas constant, J/(mol K)
\( S \) entropy, J/(mol K)
\( \text{Sh} \) Sherwood number (\( \text{Sh} = k_pL/D_s \))
\( t \) time, s
\( T \) temperature, K
\( z \) dimensionless distance

Greek Letters

\( \beta \) thermicity group, dimensionless
\( \epsilon \) dimensionless parameter related to Soret effect
\( \gamma \) Arrhenius group, dimensionless
\( \phi \) dimensionless temperature
\( \mu \) chemical potential, J/mol
\( \theta \) dimensionless composition
\( \nu \) stoichiometric coefficient
\( \rho \) density, kg/m\(^3\)
\( \tau \) dimensionless time
\( \omega \) dimensionless parameter related to Dufour effect

Subscripts

\( \text{b} \) bulk phase
\( \text{D} \) Dufour
e effective eq equilibrium
\( \text{P} \) product
\( \text{q} \) heat
\( \text{r} \) reaction
\( \text{s} \) surface
\( \text{T} \) thermal diffusion
S component S

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