Modeling of thermodynamically coupled reaction-transport systems

Yaşar Demirel *

Department of Chemical and Biomolecular Engineering, University of Nebraska Lincoln, Lincoln, NE 68588, United States

Abstract

Nonisothermal reaction-diffusion systems control the behavior of many transport and rate processes in physical, chemical and biological systems, such as pattern formation and chemical pumps. Considerable work has been published on mathematically coupled nonlinear differential equations by neglecting thermodynamic coupling between a chemical reaction and transport processes of mass and heat. This study presents the modeling of thermodynamically coupled system of a simple elementary chemical reaction with molecular heat and mass transport. The thermodynamic coupling refers that a flow occurs without or against its primary thermodynamic driving force, which may be a gradient of temperature or chemical potential or reaction affinity. The modeling is based on the linear nonequilibrium thermodynamics approach by assuming that the system is in the vicinity of global equilibrium. The modeling equations lead to unique definitions of cross-coefficients between a chemical reaction and heat and mass flows in terms of kinetic parameters, transport coefficients and degrees of coupling. These newly defined parameters need to be determined to describe some coupled reaction-transport systems. Some methodologies are suggested for the determination of the parameters and some representative numerical solutions for coupled reaction-transport systems are presented.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Balance equations; Reaction-transport systems; Thermodynamic coupling; Nonequilibrium thermodynamics; Degree of coupling

1. Introduction

Considerable work has been published on mathematically coupled nonlinear differential equations on reaction-diffusion systems in porous catalyst by neglecting the thermodynamic coupling. Here, the thermodynamic coupling refers that a flow (i.e. heat or mass flow or a reaction velocity) occurs without its primary thermodynamic driving force, or opposite to the direction imposed by its primary driving force. The principles of thermodynamics allow the progress of a process without or against its primary driving force only if it is coupled with another spontaneous process. This is consistent with the statement of second law, which states 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.

Thermodynamically coupled chemical reaction-transport systems control the behavior of many transport and rate processes in physical, chemical and biological systems, and require a through analysis accounting the induced flows by cross-effects [1–13]. More than 50 years ago, Turing [1] demonstrated that a reaction-diffusion system with appropriate nonlinear kinetics can cause instability in a homogeneous steady state and generate stable concentration patterns. Also the energy coupling in the membranes of living cells plays major role in the respiratory electron transport chain leading to synthesizing adenosine triphosphate (ATP). The ATP synthesis in turn, is matched and synchronized to cellular ATP utilization $ADP + P_i + nH_{in}^+ = ATP + H_2O + nH_{out}^+$, where 'in' and 'out' denote two phases separated by a membrane and n is the ratio H^+/ATP, showing the level of transmembrane proton transport for each ATP to be synthesized [7]. Consequently, the hydrolysis of ATP is coupled to transporting substrates and maintaining the essential thermodynamic forces of ion electrochemical gradients [2–6]. For example, Ca^{2+}-ATPase in the plasma membranes of most cells pump Ca^{2+} against a steep concentration gradient out of cytosol, while simultaneously counterport H^+ ions [5].

This study presents the modeling equations for thermodynamically and mathematically coupled system of a reversible elementary reaction with heat and mass flows. Such modeling may improve our understanding of some natural coupled processes, such as molecular pumps. The modeling is based on the linear nonequilibrium thermodynamics (LNET) formulations by assuming that the system is in the vicinity of global equilibrium (GE). Experimental investigations revealed that

* Tel.: +1 402 472 2745; fax: +1 402 4720 6989.
  E-mail address: ydemirel2@unl.edu.

Nomenclature

a_1, a_2	relations in Eq. (10)
A^*	nondimensional affinity in Eq. (53)
b	relation in Eq. (50) (mol K m^{-2} s^{-1})
C	concentration (mol m^{-3})
C_{Ss}	reactant concentration at surface (mol m^{-3})
Da	Damköhler number
$D_{D,e}$	coupling coefficient related to the Dufour effect (J m^2 mol^{-1} s^{-1})
$D_{S,e}$	effective diffusion coefficient for the substrate S (m^2 s^{-1})
$D_{T,e}$	coupling coefficient related to the Soret effect (mol m^{-1} s^{-1} K^{-1})
E	activation energy of the chemical reaction (J mol^{-1})
ΔH_r	reaction enthalpy (J mol^{-1})
J	diffusive mass flux (flow) (mol m^{-2} s^{-1})
J_q	conduction heat flux (flow) (W m^{-2})
J_r	volumetric reaction rate (mol m^{-3} s^{-1})
k_e	effective thermal conductivity (W m^{-1} K^{-1})
k_v	first order reaction rate constant (s^{-1})
L	characteristic half thickness (m)
Le	modified Lewis number
L_{ik}	phenomenological coefficients
L_{qr}	coupling coefficient between chemical reaction and heat flow (mol K m^{-2} s^{-1})
L_{Sr}	coupling coefficient between chemical reaction and mass flow (mol^2 K J^{-1} m^{-2} s^{-1})
n	number of components
N_r	number of independent reactions
t	time (s^{-1})
T	temperature (K)
V	total volume of membrane (m^3)
x	ratio of forces
X	thermodynamic force
z	dimensionless distance

Greek letters

Φ	volumetric entropy generation rate (W m^{-3} K^{-1})
α_e	effective thermal diffusivity (m^2 s^{-1})
β	thermicity group Eq. (15), dimensionless
ε	dimensionless parameter related to Soret effect in Eq. (52)
γ	Arrhenius group Eq. (51)
η	effectiveness, efficiency
φ	dimensionless temperature in Eq. (15)
κ	dimensionless parameter in Eq. (53)
λ_S	relation in Eq. (17) (J m^3 mol^{-2})
μ	chemical potential
θ	dimensionless concentration in Eq. (10)
ρ	density (kg m^{-3})
σ	dimensionless parameter in Eq. (52)
τ	dimensionless time in Eq. (51)
ω	dimensionless parameter related to Dufour effect in Eq. (53)

Subscripts

D	Dufour
e	effective
eq	equilibrium
q	heat
r	reaction
s	surface
S	Soret
T	thermal diffusivity

LNET is capable of describing thermodynamically coupled processes of oxidative phosphorylation, mitochondrial H$^+$ pumps and (Na$^+$ and K$^+$)-ATPase, because mainly due to enzymatic feedback [2–5]. Moreover, the LNET formulation does not require the detailed mechanism of the coupling [4,5,15–18]. Kinetic descriptions and considerations may lead to a loss of the generality characteristics of thermodynamic formulations, since the kinetics is based on specific models [3]. The modeling equations have produced some unique parameters related to cross-coefficients between scalar process of chemical reaction and vectorial processes of heat and mass flows. These parameters combine the kinetic parameters, transport coefficients and degrees of thermodynamic coupling, and relate the cross-interactions to measurable quantities. Some representative solutions of coupled reaction-transport systems by Mathematica are presented.

2. Background

2.1. Balance equations

We consider a reversible homogeneous elementary reaction between a substrate (S) and a product (P) $S \underset{k_b}{\overset{k_f}{\rightleftarrows}} P$, where k_f and k_b are the forward and backward reaction rate constants, respectively. This type of reaction system is common in chemical and biological systems, such as unimolecular isomerization [17], enzyme kinetics [2] and racemization of molecules with mirror-image structures [18]. The well known balance equations are

$$\frac{\partial C_S}{\partial t} = -\nabla \mathbf{J}_S + \nu_S J_r \tag{1}$$

$$\frac{\partial C_P}{\partial t} = -\nabla \mathbf{J}_P + \nu_P J_r \tag{2}$$

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \mathbf{J}_q + (-\Delta H_r) J_r \tag{3}$$

where $\mathbf{J}_q$ is the vector of reduced heat flow $\mathbf{J}_q = \mathbf{q} - \sum_{i=1}^{n} \mathbf{J}_i H_i$, $\mathbf{q}$ the total heat flow, H_i the partial molar enthalpy of species i and ΔH_r is the heat of reaction. The reaction velocity is $dC_S/\nu_S \, dt = dC_P/\nu_P \, dt = J_r$ and the parameters ν_S and ν_P are the stoichiometric coefficients, which are negative for reactants ($\nu_S = -1$). By using the Fick and Fourier laws in one-dimensional domain of *y*-direction and neglecting any ther-

modynamic coupling, Eqs. (1)–(3) become

$$\frac{\partial C_S}{\partial t} = D_{S,e} \frac{\partial^2 C_S}{\partial y^2} + \nu_S J_r \tag{4}$$

$$\frac{\partial C_P}{\partial t} = D_{P,e} \frac{\partial^2 C_P}{\partial y^2} + \nu_P J_r \tag{5}$$

$$\rho c_p \frac{\partial T}{\partial t} = k_e \frac{\partial^2 T}{\partial y^2} + (-\Delta H_r) J_r \tag{6}$$

where $D_{i,e}$ is the effective diffusivity for component i and k_e is the effective thermal conductivity. For a simple slab geometry shown in Fig. 1, the initial and boundary conditions are

$$t = 0: \quad C_S = C_{So}, \qquad C_P = C_{Po}, \qquad T = T_o \tag{7}$$

$$y = \pm L: \quad C_S = C_{Ss}, \qquad C_P = C_{Ps},$$

$$T = T_s \quad \text{(surface conditions)} \tag{8}$$

$$y = 0: \quad \frac{\partial C_S}{\partial y} = \frac{\partial C_P}{\partial y} = \frac{\partial T}{\partial y} = 0 \quad \text{(symmetry conditions)} \tag{9}$$

where L is the half thickness of the slab. Diffusion may reduce averaged rates relative to that obtained if the concentration was everywhere C_{Ss}. This limitation is quantified as the effectiveness factor η, and expressed as $\eta = (1/V)(\int J_r(C_i)\,dV)/J_r(C_{is})$, where V is the volume [19].

At stationary state, eliminating the reaction terms from Eqs. (4) and (5), and integrating twice with the boundary conditions given above, concentrations of the species are related to each other by

$$\theta_P = a_1 + a_2(1 - \theta_S) \tag{10}$$

where

$$\theta_S = \frac{C_S}{C_{Ss}}, \qquad \theta_P = \frac{C_P}{KC_{Ss}}, \qquad a_1 = \frac{C_{Ps}}{KC_{Ss}}, \qquad a_2 = \frac{D_{S,e}}{KD_{P,e}}$$
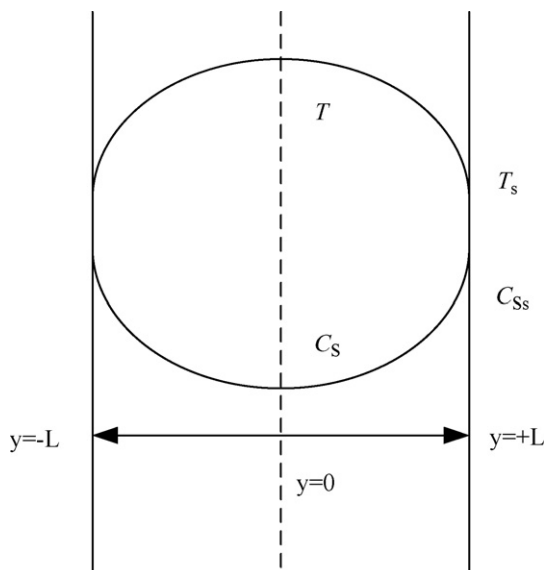

Fig. 1. Schematic temperature and concentration profiles in a thin film.

where K is the chemical reaction equilibrium constant. The value of a_1 determines the direction of reaction; the net reaction is towards the P if $a_1 < 1$. After relating the two concentrations by Eq. (10), at stationary state Eq. (4) becomes

$$\frac{d^2\theta_S}{dz^2} = (Da_S + Da_P)\theta_S - (Da_S a_1 + Da_P) \tag{11}$$

with the boundary conditions

$$\theta_S(\pm L) = 1, \qquad \frac{d\theta_S}{dz}(0) = 0 \tag{12}$$

where $z = \frac{y}{L}$

$$Da_S = \frac{k_f L^2}{D_{S,e}}, \qquad Da_P = \frac{k_b L^2}{D_{P,e}}$$

Da_S and Da_P are the Damköhler numbers and represent the ratios of the forward and backward reaction rates to the diffusion velocities ($D_{i,e}/L$). Therefore, they measure the intrinsic rates of the reactions relative to that of the diffusions, and represent an interaction between reaction and diffusion [20]. If the reaction is very fast, Damköhler number is large. For the product (P), an expression similar to Eq. (11) can also be derived. Fig. 2 displays the concentration profiles of the species of S and P at two different set of Damköhler numbers and $a_1 = 0.5$. When Da_S and Da_P are very large the concentrations of species S and P reach their equilibrium values within most of the film, and the approximate values of equilibrium concentrations become [20]

$$\theta_{S,eq} \approx \theta_{P,eq} \approx \frac{a_1 + (Da_P/Da_S)}{1 + (Da_P/Da_S)} \tag{13}$$

The relative diffusivities through the ratio of Damköhler numbers affect the equilibrium concentrations. Near the exposed surface ($z = 0$) the dimensional thickness of nonequilibrium region δ is proportional to the sum of the Damköhler numbers [20], and nondimensional nonequilibrium thickness z' is proportional to ratio of reaction rate and effective diffusivity and
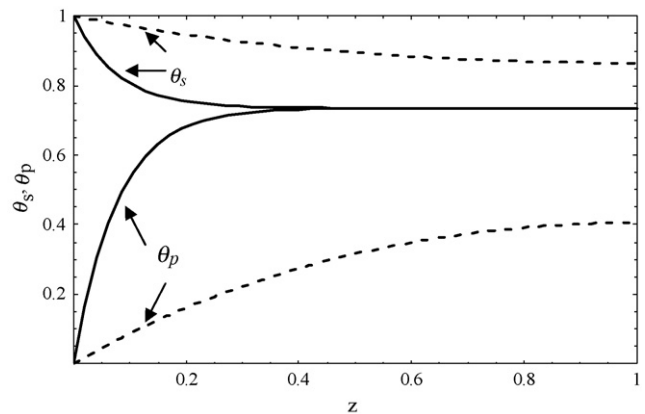

Fig. 2. Concentration profiles for diffusion in a film with a reversible reaction. Bold line $Da_S = 90$, $Da_P = 80$, $a_1 = 0.5$. Dashed line $Da_S = 1.0$, $Da_P = 1.0$, $a_1 = 0.5$.

independent of the thickness L

$$z' = \frac{\delta}{L} \sim \frac{1}{\sqrt{Da_S + Da_P}} \sim \frac{1}{\sqrt{k/D_e}} \qquad (14)$$

For large values of Damköhler numbers, the effectiveness becomes $\eta \sim 1/\sqrt{Da}$ [19].

By eliminating of the reaction terms from Eqs. (4) and (6) and integrating twice with the known boundary conditions, the temperature is related to the concentration by

$$\varphi = 1 + \beta(1 - \theta_S) \qquad (15)$$

where

$$\varphi = \frac{T}{T_s}, \qquad \beta = \frac{(-\Delta H_r)D_{S,e}C_{Ss}}{(-\nu_S)k_e T_s}$$

The value of β is a measure of nonisothermal effects; as β approaches zero, system becomes isothermal.

2.2. Phenomenological equations

Reaction-diffusion systems with heat effects represent open and nonequilibrium systems with thermodynamic forces of temperature gradient, concentration gradient and affinity. For the chemical reaction-transport system the local rate of entropy production is [8,21]

$$\Phi = \mathbf{J}_q \nabla \left(\frac{1}{T} \right) - \mathbf{J}_S \frac{(\nabla \mu_S)_{T,P}}{T}$$
$$- \mathbf{J}_P \frac{(\nabla \mu_P)_{T,P}}{T} + J_{rS} \frac{A}{T} \geq 0 \qquad (16)$$

where $(\nabla \mu_i)_{T,P} = \sum_{i=1}^{n-1} (\partial \mu_i / \partial C_i) \nabla C_i$. By using the Gibbs–Duhem equation at constant temperature and pressure $(C_S \nabla \mu_S + C_P \nabla \mu_P = 0)$ and no volume flow condition $(\mathbf{J}_S V_S + \mathbf{J}_P V_P = 0)$, where V_i is the partial molar volume of species i, Eq. (16) becomes

$$\Phi = -\mathbf{J}_q \left(\frac{1}{T^2} \right) \nabla T - \mathbf{J}_S \frac{1}{T} \lambda_S \nabla C_S + J_{rS} \frac{A}{T} \geq 0 \qquad (17)$$

where

$$\lambda_S = \left(1 + \frac{C_S}{C_P} \right) \left(\frac{\partial \mu_S}{\partial C_S} \right)_{T,P}, \qquad \text{for } (V_S \approx V_P)$$

where $\mathbf{J}_i$ is the vector of mass flows, μ_i the chemical potential of species i and A is the affinity $(A = -\sum \nu_i \mu_i)$. Eq. (17) consists of scalar processes of chemical reactions and vectorial processes of heat and mass flows, while it excludes viscous, electrical, and magnetic effects. Eq. (17) identifies the following independent conjugate flows J_i and forces X_k to be used in the linear phenomenological equations (PEs) when the system is in the vicinity of GE

$$\mathbf{J}_S = -L_{SS} \frac{1}{T} \lambda_S \nabla C_S - L_{Sq} \frac{1}{T^2} \nabla T + \mathbf{L}_{Sr} \frac{A}{T} \qquad (18)$$

$$\mathbf{J}_q = -L_{qS} \frac{1}{T} \lambda_S \nabla C_S - L_{qq} \frac{1}{T^2} \nabla T + \mathbf{L}_{qr} \frac{A}{T} \qquad (19)$$

$$J_r = -\mathbf{L}_{rS} \frac{1}{T} \lambda_S \nabla C_S - \mathbf{L}_{rq} \frac{1}{T^2} \nabla T + L_{rr} \frac{A}{T} \qquad (20)$$

2.3. The phenomenological coefficients

The phenomenological coefficients L_{ik} appearing above are related by various constraints, such as Onsager's reciprocity, Gibbs–Duhem equation at equilibrium, and the choice of reference frame for diffusivities. The type the constraints, on the other hand, depends on the choice of conjugate flows and forces, and frame of reference. Due to Onsager's reciprocal rules $(L_{ik} = L_{ki})$ the number coefficients to be determined would be six instead of nine when the conjugate flows and forces are identified by a proper entropy generation relation and the flows are related to the forces linearly.

Onsager's reciprocal relations states that $L_{ik} = L_{ki}$ if J_i and J_k have the same parity under time reversal and $L_{ik} = -L_{ki}$ if J_i and J_k have the opposite parity. In the absence of pertinent symmetries or invariances, all types of cross-couplings are possible and lead to nonvanishing cross-coefficients L_{ik}. If the structure of the system is invariant with respect to some or all of the orthogonal transformations, then the invariance will eliminate certain cross-couplings and their cross-coefficients will vanish. If these symmetries are not exact then the corresponding cross-couplings would be weak and negligible. Of course the discussions above are valid only if the entropy production relation is properly derived using the correct and specific physics of a system considered [22].

For the nonvanishing cross-coefficients L_{ik}, all the forces contribute for each flow. Here, Eqs. (18)–(20) take into account the thermodynamic couplings between vectorial processes and between vectorial and scalar processes, which is possible in an anisotropic medium according to the Curie–Prigogine principle [15]. Curie–Prigogine principle states that "macroscopic causes always have fewer or equal symmetries than the effects they produce." Therefore, a scalar thermodynamic force such as chemical affinity, which has the high symmetry of isotropy, cannot cause a diffusion flow, which has lower symmetry because of its directionality. We can also state that a scalar cause cannot produce a vectorial effect, and generally, irreversible processes of different tensorial character (scalars, vectors and higher-order tensors) do not couple with each other. Therefore, the cross-coefficients $\mathbf{L}_{Sr}$, $\mathbf{L}_{rS}$, $\mathbf{L}_{qr}$ and $\mathbf{L}_{rq}$ would vanish in isotropic media (as commonly assumed) or would have vectorial character due to morphology of the interface, which separates reactants and products or due to compartmental structure causing an anisotropic character. For example, in active transport in biological cells, the hydrolysis of ATP is coupled with the flow of sodium ions outside of the cell. The flow direction is controlled by the structure of the membrane and coupling mechanisms in mitochondria. The medium may be locally isotropic, although it is not spatially homogenous. In this case, the coupling coefficients are associated with the whole system [2].

2.4. The degrees of couplings

The cross-coefficients determine the degrees of couplings between the pair of flows

$$r_{\text{Sq}} = \frac{L_{\text{Sq}}}{(L_{\text{SS}}L_{\text{qq}})^{1/2}}, \qquad \mathbf{r}_{\text{Sr}} = \frac{\mathbf{L}_{\text{Sr}}}{(L_{\text{SS}}L_{\text{rr}})^{1/2}},$$

$$\mathbf{r}_{\text{rq}} = \frac{\mathbf{L}_{\text{rq}}}{(L_{\text{rr}}L_{\text{qq}})^{1/2}} \tag{21}$$

Here, r_{Sq} is the degree of coupling between heat and mass flows, $\mathbf{r}_{\text{Sr}}$ between chemical reaction and heat flow and $\mathbf{r}_{\text{rq}}$ is between chemical reaction mass flow. The vectorial character of the degrees of couplings $\mathbf{r}_{\text{Sr}}$ and $\mathbf{r}_{\text{rq}}$ may reflect the morphological and/or compartmental structure of medium where couplings occur as well as the properties of the cross-coefficients $\mathbf{L}_{\text{Sr}}$ and $\mathbf{L}_{\text{rq}}$ [2,5,8,15,16,18].

2.5. Determination of the coefficients

The diagonal elements of the phenomenological coefficients L_{ik} matrix $\mathbf{L}$ may be identified using the Fick, Fourier and the mass action laws. Comparison of the first term on the rhs of Eq. (18) with Fick's law ($\mathbf{J} = -D_{\text{S,e}}\nabla C_{\text{S}}$) yields $L_{\text{SS}} = D_{\text{S,e}}T/\lambda_{\text{S}}$. Similarly, comparison of the second term on the rhs of Eq. (19) with Fourier's law ($\mathbf{J}_q = -k_e\nabla T$) yields $L_{\text{qq}} = k_eT^2$. The cross-coefficients (L_{Sq} or L_{qS}) may be represented by the Soret coefficient (s_{T}) or the thermal diffusion coefficient (D_{T}), which are related to each other by $L_{\text{Sq}} = s_{\text{T}}D_{\text{S,e}}T^2C_{\text{S}} = D_{\text{T}}T^2C_{\text{S}}$. The Soret coefficient is the ratio of thermal diffusion coefficient to ordinary diffusion coefficient ($S_{\text{T}} = D_{\text{T}}/D_{\text{S,e}}$) at steady state. The Soret coefficient changes in the range 10^{-2} to $10^{-3}\,\text{K}^{-1}$ for gases, nonelectrolytes and electrolytes, however it might be larger for polymer solutions [18,23]. The L_{qS} ($=D_{\text{T}}T^2C_{\text{S}}$) may be expressed by the Dufour coefficient D_{D} $L_{\text{qS}} = D_{\text{D}}C_{\text{S}}T/\lambda_{\text{S}}$. For $L_{\text{qS}} = L_{\text{Sq}}$, we have $D_{\text{D}} = D_{\text{T}}T\lambda_{\text{S}}$, which is proved experimentally [18]. For liquids, the diffusion coefficient D is of the order of $10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ and the thermal diffusion coefficient D_{T} is of the order of 10^{-8} to $10^{-10}\,\text{cm}^2\,\text{s}^{-1}\,\text{K}$. For gases, the order of magnitude for D and D_{T} is $10^{-1}\,\text{cm}^2\,\text{s}^{-1}$ and 10^{-4} to $10^{-6}\,\text{cm}^2\,\text{s}^{-1}\,\text{K}$, respectively [18,21,24].

We may define two new effective diffusion coefficients of ($D_{\text{T,e}}$ and $D_{\text{D,e}}$) that are related to the thermal diffusion and the Dufour effect, respectively

$$D_{\text{T,e}} = L_{\text{Sq}}\frac{1}{T^2} = s_{\text{T}}D_{\text{S,e}}C_{\text{S}} = D_{\text{T}}C_{\text{S}} \tag{22}$$

$$D_{\text{D,e}} = L_{\text{qS}}\frac{\lambda_{\text{S}}}{T} = D_{\text{D}}C_{\text{S}} \tag{23}$$

As the general transport equations are for an anisotropic medium to support the thermodynamic coupling between the scalar and the vectorial processes, the transport coefficients such as k and D become tensors of the second rank $\boldsymbol{\kappa}$ and $\mathbf{D}$ [8,18,20]. Here the effective transport coefficients incorporating the effects of the medium are taken into account for the simplicity.

2.6. Reaction velocity

The affinity for the reaction considered is $A = \mu_{\text{S}} - \mu_{\text{P}}$. The reaction velocity J_{r} in terms of affinity is [8,16,18]

$$J_{\text{r}} = J_{\text{rf}}\left(1 - \exp\left(-\frac{A}{RT}\right)\right) \tag{24}$$

where $J_{\text{rf}} = k_{\text{f}}C_{\text{S}}$. If we expand Eq. (24) at near GE state, which may be specified by the inequality $|A/RT| \ll 1$, then we have an approximate linear relationship between the reaction velocity and the chemical affinity for an elementary reaction

$$J_{\text{r}} = \frac{J_{\text{rf,eq}}}{R}\frac{A}{T} \tag{25}$$

Thus, an elementary reaction rate is uniquely defined by the corresponding affinity since $J_{\text{rf,eq}}$ becomes constant due to uniform concentration at equilibrium when a system is in the vicinity of GE with fast diffusion and heat conduction processes. Comparing the third term on the right of Eq. (20) with Eq. (25), the coefficient L_{rr} is defined by

$$L_{\text{rr}} = \frac{J_{\text{rf,eq}}}{R} = \frac{k_{\text{f}}C_{\text{S,eq}}}{R} = \frac{k_{\text{o}}\exp(-E_{\text{f}}/RT)C_{\text{S,eq}}}{R} \tag{26}$$

where k_{o} is the frequency and E_{f} is the activation energy for the forward reaction. The L_{rr} is dependent on the rate constant and consequently on the equilibrium concentration $C_{\text{S,eq}}$ and the amount of chemical catalyst.

Linear flow-force relations are valid when the Gibbs free energy ranges less than $1.5\,\text{kJ}\,\text{mol}^{-1}$ for chemical reactions [15,18]. However, some selected biological pathways occur at near GE conditions [2,3], and for some chemical reactions, the formalism of LNET can be used in wider ranges than usually expected [14,25–28]. By conservation of mass, some flow-force relations of enzyme catalyzed and other chemical reactions can be described by a simple hyperbolic-tangent function. Therefore, a plot of reaction velocity versus affinity has three regions; the regions at very high positive and negative values of affinity, the reaction velocity is almost independent of affinity. In between, however, the reaction velocity varies smoothly leading to a quasi-linear region around the inflection point. This region extends the linear flow-force relations over a $7\,\text{kJ}\,\text{mol}^{-1}$ with an error in the reaction velocity less than 15%. This behavior is independent of the reaction rate constants, and mainly occurs due to conservation conditions [27].

2.7. The modified phenomenological equations

With these newly defined primary and cross-coefficients, Eqs. (18)–(20) become

$$\mathbf{J}_{\text{S}} = -D_{\text{S,e}}\nabla C_{\text{S}} - D_{\text{T,e}}\nabla T + \mathbf{L}_{\text{Sr}}\frac{A}{T} \tag{27}$$

$$\mathbf{J}_q = -D_{\text{D,e}}\nabla C_{\text{S}} - k_e\nabla T + \mathbf{L}_{\text{qr}}\frac{A}{T} \tag{28}$$

$$J_{\text{r}} = -\mathbf{L}_{\text{rS}}\frac{1}{T}\lambda_{\text{S}}\nabla C_{\text{S}} - \mathbf{L}_{\text{rq}}\frac{1}{T^2}\nabla T + \frac{k_{\text{f}}C_{\text{S,eq}}}{R}\frac{A}{T} \tag{29}$$

2.8. Determination of cross-coefficients for reaction-transport system

If 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 by the following relations

$$\mathbf{L}_{rS} = \mathbf{L}_{Sr} = \left(\frac{\mathbf{J}_S}{A/T} \right)_{\nabla C_S = 0, \nabla T = 0}$$
$$= \left(\frac{\partial \mathbf{J}_S}{\partial(A/T)} \right)_{\nabla C_S, \nabla T} \cong \left(\frac{\Delta \mathbf{J}_S}{\Delta(A/T)} \right)_{\nabla C_S, \nabla T} \quad (30)$$

$$\mathbf{L}_{rq} = \mathbf{L}_{qr} = \left(\frac{\mathbf{J}_q}{A/T} \right)_{\nabla C_S = 0, \nabla T = 0}$$
$$= \left(\frac{\partial \mathbf{J}_q}{\partial(A/T)} \right)_{\nabla C_S, \nabla T} \cong \left(\frac{\Delta \mathbf{J}_q}{\Delta(A/T)} \right)_{\nabla C_S, \nabla T} \quad (31)$$

For a closed system at stationary state $\mathbf{J}_S = 0$, we have

$$\mathbf{J}_S = 0 = -D_{S,e}\nabla C_S - D_{T,e}\nabla T + \mathbf{L}_{Sr}\frac{A}{T} \quad (32)$$

$$\mathbf{L}_{Sr} = \left(D_{S,e}\frac{\nabla C_S}{A/T} + D_{T,e}\frac{\nabla T}{A/T} \right) = \mathbf{L}_{rS} \quad (33)$$

Using $A = RT\ln(J_{rf}/J_{rb})$ in Eq. (33), we get

$$\mathbf{L}_{Sr} = \frac{1}{R\ln(J_{rf}/J_{rb})}(D_{S,e}\nabla C_S + D_{T,e}\nabla T) = \mathbf{L}_{rS} \quad (34)$$

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

$$J_r = 0 = -\mathbf{L}_{rS}\frac{1}{T}\lambda_S\nabla C_S - \mathbf{L}_{rq}\frac{1}{T^2}\nabla T \quad (35)$$

and the two coupling coefficients are related to each other by

$$\mathbf{L}_{rq} = -\mathbf{L}_{rS}T\lambda_S\frac{\nabla C_S}{\nabla T} = \mathbf{L}_{qr} \quad (36)$$

By using the relationship $-C_S s_T = \nabla C_S / \nabla T$ at steady state, the coefficient $\mathbf{L}_{rq}$ in terms of the Soret coefficient s_T becomes

$$\mathbf{L}_{rq} = \mathbf{L}_{rS}T\lambda_S C_S s_T \quad (37)$$

Using Eq. (34) in Eq. (37), we find

$$\mathbf{L}_{rq} = \frac{T\lambda_S C_S s_T}{A/T}[D_{S,e}\nabla C_S + D_{T,e}\nabla T] \quad (38)$$

Eqs. (34) and (38) suggest that the cross-coefficients $\mathbf{L}_{rq}$ and $\mathbf{L}_{rS}$ 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.

3. Coupled system of chemical reaction and heat and mass flows

By inserting Eqs. (27)–(29) into Eq. (1) and Eq. (3), we may describe the thermodynamically and mathematically coupled system of chemical reaction and heat and mass flows

$$\frac{\partial C_S}{\partial t} = -\nabla\left(-D_{S,e}\nabla C_S - D_{T,e}\nabla T + \mathbf{L}_{Sr}\frac{A}{T} \right)$$
$$- \left(-\mathbf{L}_{rS}\frac{\lambda_S}{T}\nabla C_S - \frac{\mathbf{L}_{rq}}{T^2}\nabla T + \frac{k_f C_{S,eq}}{R}\frac{A}{T} \right) \quad (39)$$

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla\left(-D_{D,e}\nabla C_S - k_e\nabla T + \mathbf{L}_{qr}\frac{A}{T} \right)$$
$$+ (-\Delta H_r)\left(-\mathbf{L}_{rS}\frac{\lambda_S}{T}\nabla C_S - \frac{\mathbf{L}_{rq}}{T^2}\nabla T + \frac{k_f C_{S,eq}}{R}\frac{A}{T} \right) \quad (40)$$

Under mechanical equilibrium, we have

$$\nabla\left(\frac{\mu_i}{T} \right) = \left[\mu_i - T\left(\frac{\partial \mu_i}{\partial T} \right) \right]\nabla\left(\frac{1}{T} \right) + \frac{(\nabla\mu_i)_T}{T}$$
$$= -H_i\frac{\nabla T}{T^2} + \frac{(\nabla\mu_i)_T}{T} \quad (41)$$

where H_i is the partial enthalpy of species i. By using the definition of affinity ($A = \mu_S - \mu_P$) and Eq. (41) for the two components S and P with the Gibbs–Duhem equation ($C_S\nabla\mu_S + C_P\nabla\mu_P = 0$) and the following relations $\lambda_S = (1 + C_S/C_P)(\partial\mu_S/\partial C_S)_{T,P}$ (for $V_S = V_P$), $\Delta G_r^o + T\Delta S_r = \Delta H_r$ we obtain

$$\nabla\left(\frac{A}{T} \right) = \left(\nabla\left(\frac{\mu_S}{T} \right) - \nabla\left(\frac{\mu_P}{T} \right) \right) = \frac{\lambda_S}{T}\nabla C_S - \frac{-\Delta H_r}{T^2}\nabla T \quad (42)$$

Substituting Eq. (42) in Eqs. (39) and (40), we have

$$\frac{\partial C_S}{\partial t} = D_{S,e}\nabla^2 C_S + D_{T,e}\nabla^2 T + \frac{\mathbf{L}_{rq} + \mathbf{L}_{Sr}(-\Delta H_r)}{T^2}\nabla T$$
$$- \frac{k_f C_{S,eq}}{R}\frac{A}{T} \quad (43)$$

$$\rho c_p\frac{\partial T}{\partial t} = D_{D,e}\nabla^2 C_S + k_e\nabla^2 T - \frac{\lambda_S[(-\Delta H_r)\mathbf{L}_{rS} + \mathbf{L}_{qr}]}{T}\nabla C_S$$
$$+ \frac{(-\Delta H_r)k_f C_{S,eq}}{R}\frac{A}{T} \quad (44)$$

where the group (A/RT) is the dimensionless affinity A^* and may be expressed by

$$A^* = \frac{A}{RT} = \ln K(T) + \ln\left(\frac{a_S}{a_P} \right) = \ln\left(\frac{k_f}{k_b} \right) + \ln\left(\frac{C_S}{C_P} \right) \quad (45)$$

In Eq. (45), the activities of a_S and a_P are assumed to be equal to concentrations C_S and C_P, respectively, by neglecting the non-ideality effects on the species. Using the Arrhenius equations, we have

$$\ln\left(\frac{k_f}{k_b} \right) = \frac{E_b - E_f}{RT} \quad (46)$$

Using Eq. (46), we reduce Eqs. (43) and (44) to

$$\frac{\partial C_S}{\partial t} = D_{S,e}\nabla^2 C_S + D_{T,e}\nabla^2 T + \frac{L_{rq} + L_{Sr}(-\Delta H_r)}{T^2}\nabla T$$
$$- \left[C_{S,eq}k_o\exp\left(\frac{-E_f}{RT}\right)\right]\left(\frac{E_b - E_f}{RT} + \ln\left(\frac{C_S}{C_P}\right)\right) \tag{47}$$

$$\rho c_p \frac{\partial T}{\partial t} = D_{D,e}\nabla^2 C_S + k_e\nabla^2 T - \frac{\lambda_S[(-\Delta H_r)L_{rS} + L_{qr}]}{T}\nabla C_S$$
$$+(-\Delta H_r)\left[C_{S,eq}k_o\exp\left(\frac{-E_f}{RT}\right)\right]$$
$$\times\left(\frac{E_b - E_f}{RT} + \ln\left(\frac{C_S}{C_P}\right)\right) \tag{48}$$

One-dimensional forms of Eqs. (47) and (48) in the *y*-direction are

$$\frac{\partial C_S}{\partial t} = D_{S,e}\frac{\partial^2 C_S}{\partial y^2} + D_{T,e}\frac{\partial^2 T}{\partial y^2} + \frac{b}{T^2}\frac{\partial T}{\partial y}$$
$$- \left[C_{S,eq}k_o\exp\left(\frac{-E_f}{RT}\right)\right]\left(\frac{E_b - E_f}{RT} + \ln\left(\frac{C_S}{C_P}\right)\right) \tag{49}$$

$$\frac{\partial T}{\partial t} = \frac{D_{D,e}}{\rho c_p}\frac{\partial^2 C_S}{\partial y^2} + \alpha_e\frac{\partial^2 T}{\partial y^2} - \frac{\lambda_S b}{\rho c_p T}\frac{\partial C_S}{\partial y}$$
$$+ \frac{-\Delta H_r}{\rho c_p}\left[C_{S,eq}k_o\exp\left(\frac{-E_f}{RT}\right)\right]$$
$$\times\left(\frac{E_b - E_f}{RT} + \ln\left(\frac{C_S}{C_P}\right)\right) \tag{50}$$

where

$$b = L_{rq} + L_{Sr}(-\Delta H_r) = L_{rr}[L_{qq}r_{rq}^2 + L_{SS}r_{Sr}^2(-\Delta H_r)]$$
$$= \frac{k_f C_{S,eq}T}{R}\left(k_e T r_{rq}^2 + \left(\frac{D_{S,e}}{\lambda_S}\right)r_{Sr}^2(-\Delta H_r)\right)$$

Eqs. (49) and (50) use the same initial and boundary conditions given in Eqs. (7)–(9). With the following parameters

$$z = \frac{y}{L}, \qquad \tau = \frac{D_{S,e}t}{L^2}, \qquad Da_S = \frac{L^2 k_o\exp(E_f/RT_s)}{D_{S,e}},$$

$$\gamma_f = \frac{E_f}{RT_s}, \qquad \gamma_b = \frac{E_b}{RT_s}, \qquad Le = \frac{k_e/\rho C_p}{D_{S,e}} = \frac{\alpha_e}{D_{S,e}} \tag{51}$$

Nondimensional forms of Eqs. (49) and (50) become

$$\frac{\partial\theta_S}{\partial\tau} = \frac{\partial^2\theta_S}{\partial z^2} + \varepsilon\frac{\partial^2\varphi}{\partial z^2} + \frac{\sigma}{\varphi^2}\frac{\partial\varphi}{\partial z}$$
$$- A^* Da_S\theta_{S,eq}\exp\left[\gamma_f\left(1 - \frac{1}{\varphi}\right)\right] \tag{52}$$

$$\frac{1}{Le}\frac{\partial\varphi}{\partial\tau} = \frac{\partial^2\varphi}{\partial z^2} + \omega\frac{\partial^2\theta_S}{\partial z^2} - \frac{\kappa}{\varphi}\frac{\partial\theta_S}{\partial z}$$
$$+ A^* Da_S\beta\theta_{S,eq}\exp\left[\gamma_f\left(1 - \frac{1}{\varphi}\right)\right] \tag{53}$$

where

$$\varepsilon = \frac{D_{T,e}T_s}{D_{S,e}C_{Ss}}, \qquad \omega = \frac{D_{D,e}c_s}{k_e T_s},$$

$$\sigma = \frac{bL}{T_s D_{S,e}C_{Ss}} = \frac{[L_{rq} + L_{Sr}(-\Delta H_r)]L}{T_s D_{S,e}C_{Ss}}, \qquad \kappa = \frac{bC_{Ss}L\lambda_S}{k_e T_s^2}$$

and

$$A^* = \left(\frac{\gamma_b - \gamma_f}{\varphi}\right) + \ln\left(\frac{\theta_S}{K[a_1 + a_2(1 - \theta_S)]}\right);$$

The parameter b is defined in Eq. (50). These equations suggest that the degree of couplings beside the other parameters would control the evolution and stability of the system. Therefore, induced effects due to various coupling phenomena can increase the possibility that the system may evolve to multiple states and diversify its behavior [27,30]. The parameters ε, σ, ω and κ above are associated with the cross-coefficients and hence control the coupled phenomena in the *y*-direction. Specifically, the ε and ω control the coupling between mass and heat flows, while the σ and κ control the coupling between the chemical reaction and mass flow, and chemical reaction and heat flow, respectively. The initial and boundary conditions based on Eqs. (7)–(9) become

$$\begin{aligned}
&\tau = 0: &&\theta_S = \theta_{So}, \quad \theta_P = \theta_{Po}, \quad \varphi = \varphi_o\\
&z = \pm 1, \tau > 0: &&\theta_S = 1, \quad \theta_P = 1, \quad \varphi = 1\\
&z = 0, \tau > 0: &&\frac{\partial\theta_S}{\partial z} = \frac{\partial\theta_P}{\partial z} = \frac{\partial\varphi}{\partial z} = 0
\end{aligned} \tag{54}$$

Here, the nondimensional concentrations θ_S and θ_P are related approximately to each other by the relation $\theta_P = a_1 + a_2(1 - \theta_S)$, although it is derived for stationary states. Accuracy of the solutions obtained from Eqs. (52) and (53) depends on the reliable data, such as the effective transport coefficients and cross-coefficients. The parameter b in terms of the degrees of couplings r_{qr} and r_{Sr} may improve the accuracy since the degrees of couplings vary between −1 and +1. Some processes will not be dependent on some of the forces when some certain 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 [3,5].

4. Some special cases of coupled phenomena

Previously, we have considered the one-dimensional case where heat and mass flows are coupled in a reaction-diffusion system with heat effects, in which the cross-coefficients L_{rq} and L_{qr} as well as L_{rS} and L_{Sr} have vanished [21]. This means that the reaction velocity is coupled neither with the heat flow nor with the mass flow. Now we present the one-dimensional modeling for the following thermodynamically coupled systems:

(1) Coupled phenomena at stationary state.
(2) No coupling exists between the heat flow and chemical reaction: $L_{rq} = L_{qr} = 0$.
(3) No coupling exists between the mass flow and chemical reaction: $L_{rS} = L_{Sr} = 0$.

In all the systems above, heat and mass flows are still thermodynamically coupled. The modeling equations for these processes are derived and discussed briefly in the following sections.

4.1. Stationary coupling of chemical reactions with heat and mass flows

Stationary forms of Eqs. (52) and (53) are

$$0 = \frac{\partial^2 \theta_S}{\partial z^2} + \varepsilon \frac{\partial^2 \varphi}{\partial z^2} + \frac{\sigma}{\varphi^2} \frac{\partial \varphi}{\partial z} - A^* Da_S \theta_{S,eq} \exp\left[\gamma\left(1 - \frac{1}{\varphi}\right)\right] \tag{55}$$

$$0 = \frac{\partial^2 \varphi}{\partial z^2} + \omega \frac{\partial^2 \theta_S}{\partial z^2} - \frac{\kappa}{\varphi} \frac{\partial \theta_S}{\partial z} + A^* Da_S \beta \theta_{S,eq} \exp\left[\gamma\left(1 - \frac{1}{\varphi}\right)\right] \tag{56}$$

The boundary conditions are defined in Eq. (54). Using the previously derived relations $\varphi = 1 + \beta(1 - \theta_S)$ and $\theta_P = a_1 + a_2(1 - \theta_S)$ in Eq. (55), the temperature φ is related to the concentration θ_S and the concentrations θ_P and θ_S are related to each other, and we have

$$0 = (1 - \varepsilon\beta)\frac{d^2\theta_S}{dz^2} - \frac{\sigma\beta}{[1 + \beta(1 - \theta_S)]^2}\frac{d\theta_S}{dz}$$

$$- \left[\left(\frac{\gamma_b - \gamma_f}{1 + \beta(1 - \theta_S)}\right) + \ln\frac{\theta_S}{a_1 + a_2(1 - \theta_S)}\right] Da_S\theta_{S,eq}$$

$$\times \exp\left[\gamma\left(1 - \frac{1}{1 + \beta(1 - \theta_S)}\right)\right] \tag{57}$$

where the products $\varepsilon\beta$ and $\beta\sigma$

$$\beta\varepsilon = \frac{(-\Delta H_r)D_{T,e}}{(-\nu_S)k_e},$$

$$\beta\sigma = \frac{(-\Delta H_r)bL}{(-\nu_S)k_e T_s^2} = \frac{(-\Delta H_r)[L_{rq} + L_{Sr}(-\Delta H_r)]L}{(-\nu_S)k_e T_s^2}$$

represent the cross-effects due to the thermodynamic coupling at steady state. Similarly, an equation can be derived for the temperature φ.

4.2. Chemical reaction velocity coupled to mass flow: $L_{rq} = L_{qr} = 0$

This specific coupling may approximately represent the active transport in biological cells in which hydrolysis of ATP is coupled with the uphill transport of ions. Experimental investigation of biological energy coupling systems shows that LNET formulation is capable of describing mitochondrial H$^+$ pumps

[3] and helps understanding molecular slips and ion leaks of Ca^{2+} and H$^+$ [5,7].

The following rate of entropy production equation shows the two contributions when there is no heat effect [2].

$$\Phi = -\mathbf{J}_S \frac{1}{T} \lambda_S \nabla C_S + J_{rS}\frac{A}{T} = \text{mass flow} + \text{chemical reaction}$$

$$= \text{output} + \text{input} \geq 0 \tag{58}$$

For the active transport in a biological cell, the chemical reaction term ($J_{rS}(A/T)$) represents the hydrolysis of ATP, which facilitates pumping the ions opposite to the direction imposed by their thermodynamic forces, and hence we have $(-\mathbf{J}_S(1/T)\lambda_S\nabla C_S) < 0$. The efficiency of energy conversion for active transport may be related to the degree of coupling by using Eq. (58)

$$\eta = \frac{\text{output}}{\text{input}} = \frac{-\mathbf{J}_S(1/T)\lambda_S\nabla C_S}{J_{rS}(A/T)} = \frac{x[(L_{SS}/L_{rr})^{1/2}x + r_{Sr}]}{r_{Sr} + (L_{rr}/L_{SS})^{1/2}} \tag{59}$$

where x is the ratio of thermodynamic forces ($[(1/T)\lambda_S\nabla C_S/(A/T)]$). The optimal efficiency would be a function of the degree of coupling [2–4,13].

When the cross-coefficients $\mathbf{L}_{rq}$ and $\mathbf{L}_{qr}$ vanish in Eqs. (27)–(29), the PEs become

$$\mathbf{J}_S = -D_{S,e}\nabla C_S - D_{T,e}\nabla T + \mathbf{L}_{Sr}\frac{A}{T}$$

$$\mathbf{J}_q = -D_{D,e}\nabla C_S - k_e\nabla T \tag{60}$$

$$J_r = -\mathbf{L}_{rS}\frac{1}{T}\lambda_S\nabla C_S + \frac{k_o\exp(-E_f/RT)C_{S,eq}}{R}\frac{A}{T} \tag{61}$$

so that the one-dimensional balance equations are

$$\frac{\partial \theta_S}{\partial \tau} = \frac{\partial^2 \theta_S}{\partial z^2} + \varepsilon \frac{\partial^2 \varphi}{\partial z^2} + \frac{\sigma'}{\varphi^2}\frac{\partial \varphi}{\partial z}$$

$$- A^* Da_S\theta_{S,eq}\exp\left[\gamma\left(1 - \frac{1}{\varphi}\right)\right] \tag{62}$$

$$\frac{1}{Le}\frac{\partial \varphi}{\partial \tau} = \frac{\partial^2 \varphi}{\partial z^2} + \omega\frac{\partial^2 \theta_S}{\partial z^2} - \frac{\kappa'}{\varphi}\frac{\partial \theta_S}{\partial z}$$

$$+ A^* Da_S\beta\theta_{S,eq}\exp\left[\gamma\left(1 - \frac{1}{\varphi}\right)\right] \tag{63}$$

where

$$\sigma' = \frac{[L_{Sr}(-\Delta H_r)]L}{T_s D_{S,e}C_{Ss}}; \qquad \kappa' = \frac{[L_{Sr}(-\Delta H_r)]C_{Ss}L\lambda_S}{k_e T_s^2}$$

By relating the cross-coefficient to the degree of coupling r_{Sr}, the cross-coefficient L_{Sr} may be eliminated

$$L_{Sr} = r_{Sr}(L_{SS}L_{rr})^{1/2} = r_{Sr}\left(\frac{D_{S,e}T}{\lambda_s}\frac{k_fC_{S,eq}}{R}\right)^{1/2} \tag{64}$$
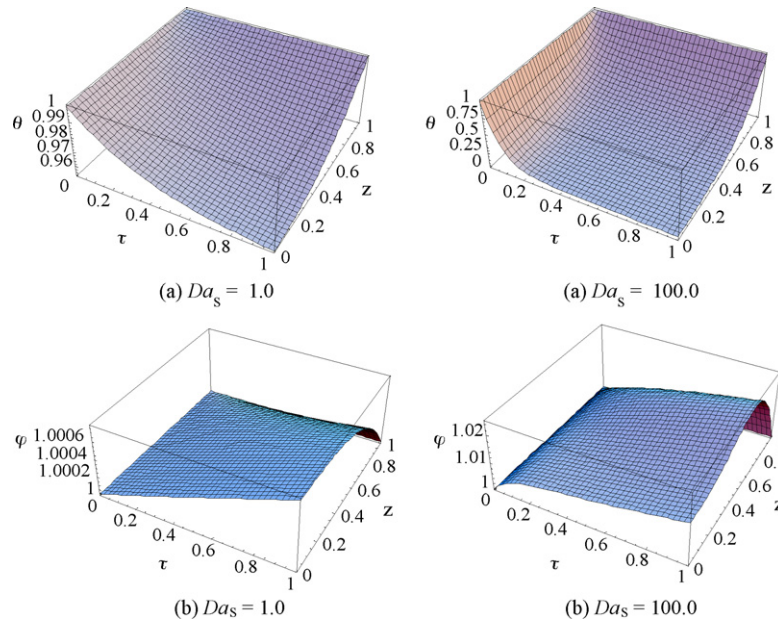
Fig. 3. Dimensionless temperature and concentration profiles obtained from Eqs. (62) and (63) with $\gamma = 27$, $\beta = 0.066$, $Le = 0.11$, $\varepsilon = 1.0$, $\omega = 0.01$, $A^* = 0.1$, $\sigma' = 0.1$, $\kappa' = 0.001$.
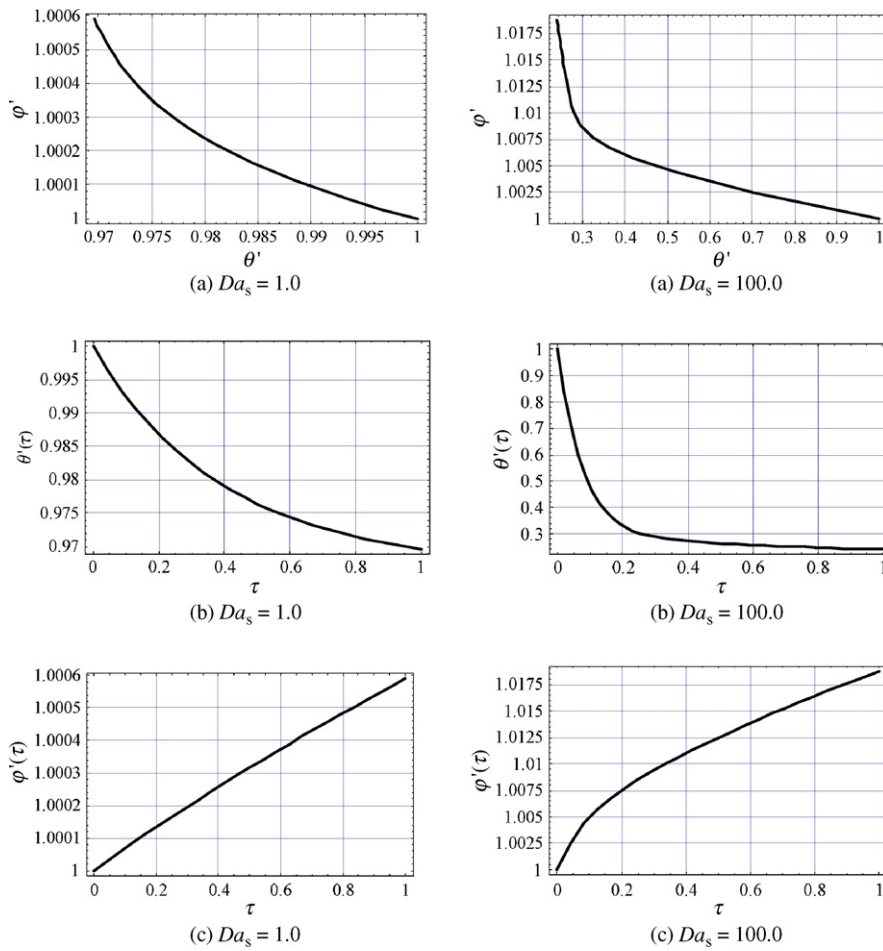

Fig. 4. Spatial integral averages obtained from Eqs. (66) and (67) using Eqs. (62) and (63): (a) change of temperature with concentration when the time varies between 0 and 1, (b) change of concentration with time and (c) change of temperature with time for $\gamma = 27$, $\beta = 0.066$, $Le = 0.11$, $\varepsilon = 1.0$, $\omega = 0.01$, $A^* = 0.1$, $\sigma' = 0.1$, $\kappa' = 0.001$.

and the parameters σ' and κ' are defined in terms of the degree of coupling r_{Sr}

$$\sigma' = r_{Sr} \left(\frac{D_{S,e}T}{\lambda_s} \frac{k_f C_{S,eq}}{R} \right)^{1/2} \frac{[(-\Delta H_r)]L}{T_s D_{S,e} C_{Ss}},$$

$$\kappa' = r_{Sr} \left(\frac{D_{S,e}T}{\lambda_s} \frac{k_f C_{S,eq}}{R} \right)^{1/2} \frac{(-\Delta H_r) C_{Ss} L \lambda_S}{k_e T_s^2} \quad (65)$$

The parameter κ' combines the forward reaction rate constant, diffusivity coefficient and thermal conductivity, and hence may reflect an 'indirect interaction' between chemical reaction and heat flow with vanishing cross-coefficients of L_{rq} and L_{qr}.

During a diffusion-controlled reaction, matter may be transported through an interface, which separates the reactants and the product. The progress of the reaction may be affected by the morphology of the interface with complicated structure, which controls the boundary conditions for the transport problem [27–29]. Morphological stability of interfaces in nonequilibrium systems may lead to self-organization and/or pattern-formation in biological, physical, chemical and geological systems [26,29]. Turing [1] demonstrated that even some simple reaction-diffusion systems could lead to spatial organizations due to instability of stationary structure depending on the activator–inhibitor interactions, control parameters and boundary conditions (see Appendix A).

4.2.1. Concentration and temperature profiles

The Mathematica is used to solve the thermodynamically coupled systems of Eqs. (62) and (63) with the maximum steps of infinity. Fig. 3 displays the dynamic behavior of the concentrations and temperatures at two different Damköhler numbers. For the fast reaction case with $Da_S = 100.0$, nonequilibrium region is considerably smaller and attained at a shorter time. For the slow reaction case with $Da_S = 1.0$, the system remains in nonequilibrium for most of the time and throughout the thickness of the film. The surfaces of temperature closely follow the change in concentrations, and reflect the effect of Damköhler numbers. As expectedly, the rise of temperature is small as the value of β is relatively small.

Since the dynamic behavior of a reaction-transport system may be more apparent with the state–space diagrams, the temperature and concentration profiles are replaced with the spatial integral averages obtained from

$$\theta'(\tau) = \int_0^1 \theta(z, \tau)\, dz \quad (66)$$

$$\varphi'(\tau) = \int_0^1 \varphi(z, \tau)\, dz \quad (67)$$

Fig. 4a compares the state–space plots of temperature versus concentration when the time changes from zero to one. Fig. 4b and c shows the changes of the spatial integral averages of temperatures and concentrations. The spatial integral average of concentration reaches its equilibrium value approximately at $\tau = 0.4$ at $Da_S = 100$. The changes are relatively sharp at $Da_S = 100.0$ while they are gradual at $Da_S = 1.0$, as expected. Fig. 5 shows the spatial integral averages of temperatures and
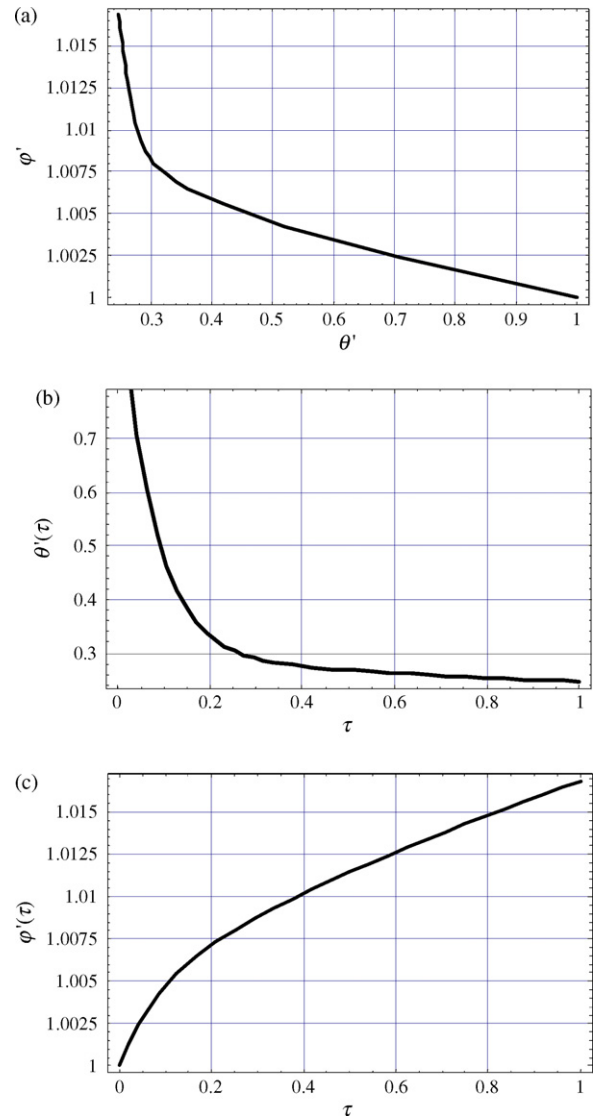

Fig. 5. Spatial averages obtained by integrating Eqs. (62) and (63) with Eqs. (66) and (67): (a) change of temperature with concentration when the time varies between 0 and 1, (b) change of concentration with time and (c) change of temperature with time for $Da_S = 100.0$, $\gamma = 27$; $\beta = 0.066$; $Le = 0.11$, $\varepsilon = 1.0$, $\omega = 0.001$, $A^* = 0.1$; $\sigma' = 0.001$; $\kappa' = 0.001$.

concentrations at $Da_S = 100$ with different values of coupling parameters. The marginal changes on the spatial integral averages of temperatures and concentrations may result from the coupling effects.

4.3. Chemical reaction velocity coupled to heat flow: $L_{Sr} = L_{rS} = 0$

The cross-coefficients $\mathbf{L}_{Sr}$ and $\mathbf{L}_{rS}$ vanish, and we have the following new PEs

$$\mathbf{J}_S = -D_{S,e} \nabla C_S - D_{T,e} \nabla T \quad (68)$$

$$\mathbf{J}_q = D_{D,e} \nabla C_S - k_e \nabla T + \mathbf{L}_{qr} \frac{1}{T} A \quad (69)$$

$$J_r = -\mathbf{L}_{rq}\frac{1}{T^2}\nabla T + \frac{k_o \exp(-E_f/RT)C_{S,eq}}{R}\frac{A}{T} \tag{70}$$

So that the one-dimensional balance equations become

$$\frac{\partial\theta_S}{\partial\tau} = \frac{\partial^2\theta_S}{\partial z^2} + \varepsilon\frac{\partial^2\varphi}{\partial z^2} + \frac{\sigma''}{\varphi^2}\frac{\partial\varphi}{\partial z}$$
$$-A^* Da_S\theta_{S,eq}\exp\left[\gamma\left(1-\frac{1}{\varphi}\right)\right] \tag{71}$$

$$\frac{1}{Le}\frac{\partial\varphi}{\partial\tau} = \frac{\partial^2\varphi}{\partial z^2} + \omega\frac{\partial^2\theta_S}{\partial z^2} - \frac{\kappa''}{\varphi}\frac{\partial\theta_S}{\partial z}$$
$$+A^* Da_S\beta\theta_{S,eq}\exp\left[\gamma\left(1-\frac{1}{\varphi}\right)\right] \tag{72}$$

where

$$\sigma'' = \frac{L_{qr}L}{T_s D_{S,e}C_{Ss}}, \qquad \kappa'' = \frac{L_{qr}C_{Ss}L\lambda_S}{k_e T_s^2}$$

By relating the parameters σ'' and κ'' and the cross-coefficient to the degree of coupling r_{qr}, we have

$$L_{qr} = r_{qr}(L_{qq}L_{rr})^{1/2} = r_{qr}\left(k_e T^2\frac{k_f C_{S,eq}}{R}\right)^{1/2} \tag{73}$$

$$\sigma'' = r_{qr}\left(k_e T^2\frac{k_f C_{S,eq}}{R}\right)^{1/2}\frac{L}{T_s D_{S,e}C_{Ss}},$$
$$\kappa'' = r_{qr}\left(k_e T^2\frac{k_f C_{S,eq}}{R}\right)^{1/2}\frac{C_{Ss}L\lambda_S}{k_e T_s^2} \tag{74}$$

The parameter σ'' combines the transport and rate coefficient of k_e, $D_{S,e}$ and k_f.

5. Conclusions

The balance equations are derived for thermodynamically and mathematically coupled system of chemical reaction and heat and mass flows. This effort may be a starting point to understand the molecular coupled phenomena between vectorial and scalar processes, such as active transport in biological cells. These modeling equations are based on the linear nonequilibrium thermodynamics approach assuming that the system is in the vicinity of global equilibrium and has anisotropic character. The equations have revealed definitions of some unique parameters related to the cross-coefficients between the scalar process of chemical reaction and the vectorial processes of heat and mass flows. These parameters combine kinetic parameters, transport coefficients, and degrees of thermodynamic couplings leading to a path for determinations of these parameters by some measurable quantities. The representative solutions of the modeling equations for the coupled chemical reaction-mass flow system are in line with the behavior of fast and slow chemical reactions in a film.

Appendix A

If we consider the change of affinity with time at constant temperature and pressure, we have

$$\frac{dA}{dt} = \left(\frac{\partial A}{\partial C_S}\right)_{T,P}\frac{dC_S}{dt} \tag{1}$$

It is possible to split the dC_S into two parts: $dC_S = d_eC_S + d_iC_S$, which are the part resulting from the exchange with the surrounding and the part due to a chemical reaction. The rate of the second part is the reaction velocity $d_iC_S/dt = \nu_S J_r$. With these relations Eq. (1) yields

$$\frac{dA}{dt} = \left(\frac{\partial A}{\partial C_S}\right)_{T,P}\frac{d_eC_S}{dt} - J_{rS}\left(\frac{\partial A}{\partial C_S}\right)_{T,P} \tag{2}$$

Eq. (2) shows that affinity changes by rate of supply of matter and chemical reaction velocity. Depending on the rate of supply, the first term in Eq. (2) may counter balance the reaction velocity, so that the affinity may become a constant. This new phenomenon represents as system where one of the forces is fixed, and may lead to a specific behavior in the evolution of the whole system [2,16].

Evolution equation, in general, is expressed by

$$\frac{\partial\mathbf{Y}}{\partial t} = f(\mathbf{Y},\lambda) \tag{3}$$

where $\mathbf{Y}$ is the column vector with the elements of the state variables $Y_1, \ldots, Y_i$, which are continuously subjected to either internal fluctuations or external perturbations. The f is mainly a nonlinear space operator and λ denotes a set of controlling parameters affecting the evolution, such as thermal conductivity, diffusivity, chemical rate constants and initial concentrations of reactants and products. The evolution equations for the dimensionless concentration θ_S and the temperature φ in the form of Eq. (3) become

$$\frac{\partial C_S}{\partial t} = f_S[C_{Ss}, C_{Ps}, T_s, \lambda(\tau, D_{S,e}, D_{P,e}, D_{T,e}, \varepsilon, \sigma, \gamma_f, A^*,$$
$$\phi_{Ss}, \theta_{S,eq}, r_{Sq}, r_{qr}, r_{Sr})] \tag{4}$$

$$\frac{\partial T}{\partial t} = f_T[C_{Ss}, C_{Ps}, T_s, \lambda(\tau, \alpha_e, \beta, D_{S,e}, \omega, \kappa, \gamma_f, \gamma_b, A^*,$$
$$\theta_{S,eq}, r_{Sq}, \mathbf{r}_{rq}, \mathbf{r}_{Sr}, -\Delta H_r, Le)] \tag{5}$$

As Eqs. (4) and (5) suggest, the degree of couplings beside the other parameters would control the evolution and stability of the system. Comparison of Eq. (4) with the simple rate expression of $dC_S/dt = -k_fC_S + k_bC_P$ alone displays the expansion in the number of controlling parameters in the coupled system of an elementary reaction with heat and mass flows. Therefore, induced cross-effects due to various coupling phenomena can

allow the system to evolve to multiple solutions and diversify its behavior depending on many controlling parameters [25,29].

References

[1] A.M. Turing, The chemical basis of morphogenesis, Philos. Trans. R. Soc. Lond. B 237 (1952) 37–72.

[2] R.S. Caplan, A. Essig, Bioenergetics and Linear Nonequilibrium Thermodynamics. The Steady State (Reprint), Harvard University Press, New York, 1999.

[3] J.W. Stucki, M. Compiani, S.R. Caplan, Efficiency of energy conversion in model biological pumps optimization by linear nonequilibrium thermodynamic relations, Biophys. Chem. 18 (1983) 101–109.

[4] Y. Demirel, S.I. Sandler, Thermodynamics of bioenergetics, Biophys. Chem. 97 (2002) 87–111.

[5] A.R. Waldeck, K. van Dam, J. Berden, P.W. Kuchel, A nonequilibrium thermodynamics model of reconstituted Ca^{2+}-ATPase, Eur. Biophys. J. 27 (1998) 255–262.

[6] Y. Demirel, S.I. Sandler, Effects of concentration and temperature on the coupled heat and mass transport in liquid mixtures, Int. J. Heat Mass Transfer 45 (2002) 75–86.

[7] P. Turina, D. Samurai, P. Graber, H^+/ATP ratio of proton transport-coupled ATP synthesis and hydrolysis catalyzed by CF0F1 ± liposomes, Eur. Mol. Biol. Org. J. 22 (2003) 418–426.

[8] Y. Demirel, Non-equilibrium Thermodynamics: Transport and Rate Processes in Physical and Biological Systems, Elsevier, Amsterdam, 2002.

[9] Q. Jin, C.M. Bethke, Kinetics of electron transfer through the respiratory chain, Biophys. J. 83 (2002) 1797–1808.

[10] R. Heinrich, S. Schuster, The modeling of metabolic systems. Structure, control and optimality, BioSystems 47 (1998) 61–77.

[11] A. Burghardt, M. Berezowski, Periodic solutions in a porous catalyst pellet-homoclinic orbits, Chem. Eng. Sci. 58 (2003) 2657–2670.

[12] P. Gas, C. Girardeaux, D. Mangelinck, A. Portavoce, Reaction and diffusion at interfaces of micro- and nanostructured materials, Mater. Sci. Eng. B 101 (2003) 43–48.

[13] Y. Demirel, S.I. Sandler, Nonequilibrium thermodynamics in engineering and science, J. Phys. Chem. B 108 (2004) 31–43.

[14] D. Reguera, J.M. Rubi, J.M.G. Vilar, The mesoscopic dynamics of thermodynamic systems, J. Phys. Chem. B 109 (2005) 21502–21515.

[15] I. Prigogine, Introduction to Thermodynamics of Irreversible Processes, third ed., Wiley, New York, 1967.

[16] S.R. De Groot, Thermodynamics of Irreversible Processes, North Holland, Amsterdam, 1966.

[17] H. Qian, D.A. Beard, Thermodynamics of stoichiometric biochemical networks in living systems far from equilibrium, Biophys. Chem. 114 (2005) 213–220.

[18] D. Kondepudi, I. Prigogine, Modern Thermodynamics; From Heat Engines to Dissipative Structures, Wiley, New York, 1999.

[19] F.G. Froment, K.B. Bischoff, Chemical Reactor Analysis and Design, Wiley, New York, 1979.

[20] W.M. Deen, Analysis of Transport Phenomena, Oxford University Press, New York, 1998.

[21] Y. Demirel, Non-isothermal reaction diffusion system with thermodynamically coupled heat and mass transfer, Chem. Eng. Sci. 61 (2006) 3379–3385.

[22] M.A. Lomholt, P.L. Hansen, L. Miao, A general theory of nonequilibrium dynamics of lipid–protein fluid membranes, Eur. Phys. J. E 16 (2005) 439–461.

[23] Y. Demirel, S.I. Sandler, Linear non-equilibrium thermodynamics theory for coupled heat and mass transport, Int. J. Heat Mass Transfer 44 (2001) 2439–2451.

[24] J. Jost, Diffusion in Solids, Liquids and Gases, Academic Press, New York, 1960.

[25] A.S. Cukrowski, A. Kolbus, On validity of linear phenomenological nonequilibrium thermodynamics equations in chemical kinetics, Acta Phys. Pol. B 36 (2005) 1485–1507.

[26] Y. Demirel, Stability of transport and rate processes, Int. J. Thermodyn. 8 (2005) 1–14.

[27] H.V. Westerhoff, K. van Dam, Thermodynamics and Control of Biological Free-energy Transduction, Elsevier, Amsterdam, 1987.

[28] O. Aono, Thermodynamic coupling of diffusion with chemical reaction, J. Stat. Phys. 13 (1975) 331–335.

[29] M. Martin, Materials in thermodynamic potential gradients, J. Chem. Thermodyn. 35 (2003) 1291–1308.

[30] M. Ruszkowski, V. Garcia-Osorio, E. Ydstie, Passivity based control of transport reaction systems, AIChE J. 51 (2005) 3147–3166.