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Thermodynamically coupled heat and mass flows in a reaction-transport system with external resistances

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ABSTRACT

Considerable work has been published on mathematically coupled nonlinear differential equations by neglecting thermodynamic coupling between heat and mass flows in reaction-transport systems. 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. This study presents the modeling of thermodynamically coupled heat and mass flows of two components in a reaction-transport system with external heat and mass transfer resistances. The modeling equations are 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 thermodynamic coupling (cross) coefficients between heat and mass flows in terms of kinetic parameters and transport coefficients. These newly defined parameters need to be determined to describe coupled reaction-transport systems. Some representative numerical solutions obtained by MATLAB illustrate the effect of thermodynamic coupling coefficients on the change of temperature and mass concentrations in time and space.

1. Introduction

Considerable work has been published on mathematically coupled nonlinear differential equations for reaction-transport 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 this process 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 purchased at the expense of a greater amount of disorganization in a series of coupled 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 [1–9]. Many published work, including some recent ones [10–12], on reaction-diffusion systems mainly consider mathematically coupled nonlinear differential relationships. More than 50 years ago, Turing [13] 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 thermodynamic coupling in the membranes of living cells plays major role in the respiratory electron transport leading to synthesizing adenosine triphosphate [6,14,15]. Another important thermodynamic coupling takes place between the hydrolysis of adenosine triphosphate and the molecular transport of substrates in active transport. The coupling between a scalar process of the hydrolysis and a vectorial process of the mass flow creates the molecular pumps responsible for uphill transport [1,14,15]. Therefore, incorporation of thermodynamic coupling into the modeling of reaction-diffusion systems, such as active transport, may be a vital step in describing these complex biochemical cycles.

Two previous studies presented the modeling equations and approximate solutions for reaction-transport systems with thermodynamic coupling between heat and mass flows [4] and between transport processes and chemical reaction [5] without external resistances. This study presents the modeling equations for thermodynamically coupled heat and mass flows in a three-component system with an elementary chemical reaction and with external transport resistances. Therefore, it is a through analysis accounting the cross effects as well as external effects. The modeling is based on the linear nonequilibrium thermodynamics (LNET) formulations by assuming that the system is in the vicinity of global equilibrium (GE). The LNET formulation does not require the detailed mechanism of the thermodynamic coupling [6,15]. The modeling equations have produced some unique parameters related to thermodynamic couplings between heat and mass flows. These parameters combine the kinetic parameters and transport coefficients and control the cross effects. Some representative

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Nomenclature

a_i	parameters in Eq. (37)
A	chemical affinity, J/mol
c_p	specific heat capacity, J/(kg K)
Da	Damköhler number
D_S	effective diffusion coefficient for the substrate S, m^2/s
D_D	coupling coefficient related to the Dufour effect, J m^2/(mol s)
D_T	coupling coefficient related to the thermal diffusion (Soret) effect, mol/(m s K)
E	activation energy of the chemical reaction, J/mol
h	heat transfer coefficient, J/(m^2 K)
h_i	partial enthalpy, J/kg
ΔH_r	reaction enthalpy, J/kg
H^E	excess specific enthalpy, J/kg
j	diffusive mass flux, mol/(m^2 s)
J_q	conduction heat flux, W/m^2
J_r	volumetric reaction rate, mol/(m^3 s)
k	effective thermal conductivity, W/(m K)
k_g	external mass transfer coefficient, m/s
k_v	first order reaction rate constant, 1/s
k_0	frequency in the Arrhenius equation, 1/s
L	characteristic half thickness, m
Le	Lewis number
L_{ik}	phenomenological coefficients
L_{qr}	element of coupling coefficient between chemical reaction and heat flow, mol K/(m^2 s)
L_{ir}	element of coupling coefficient between chemical reaction and mass flow of component *i*, mol^2 K/(J m^2 s)
n	number of components
nr	number of chemical reactions
Nu	Nusselt number
Q_i^*	heats of transport for component *i*, kJ/kg
R	gas constant, J/(mol K)
Sh	Sherwood number
t	time, s
T	temperature, K
w_i	mass fraction of component *i*
X	thermodynamic force
z	dimensionless distance

Greek letters

β	thermicity group, dimensionless
β'_S	thermicity group for thermodynamically coupled processes, dimensionless
ε	dimensionless parameter related to Soret effect in Eq. (42)
Φ	volumetric entropy generation rate, W/(m^3 K)
γ	Arrhenius group, dimensionless
ϕ	dimensionless temperature, Eq. (40)
φ	diffusivity ratios, Eq. (42)
μ	chemical potential, J/mol
θ	dimensionless composition, Eq. (40)
λ	relation in Eq. (16)
ν	stoichiometric coefficient
ρ	density, kg/m^3
τ	dimensionless time
ω	dimensionless parameter related to Dufour effect in Eq. (42)

Subscripts

D	Dufour
eq	equilibrium
P	product
q	heat
r	reaction
s	surface
T	thermal diffusion

solutions of thermodynamically and mathematically coupled partial differential equations are presented to illustrate the effects of coupling on the behavior of temperature and mass concentrations in time and space.

2. Modeling equations

We consider a single porous catalyst pellet that catalyzes the elementary reaction $\nu_S S + \nu_B B \rightarrow \nu_P P$ with a first order kinetics based on the S. The well known balance equations are

$$\rho \frac{\partial w_S}{\partial t} = -\nabla \cdot \mathbf{j}_S + \nu_S J_r \tag{1}$$

$$\rho \frac{\partial w_B}{\partial t} = -\nabla \cdot \mathbf{j}_B + \nu_B J_r \tag{2}$$

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{J}_q + (-\Delta H_r) J_r + \rho \sum_{i=1}^{2} \sum_{j=1}^{2} H_{jj}^E D_{ji} \nabla w_i \nabla w_j \tag{3}$$

where

$$\rho D_{il} = \sum_{j=1}^{2} L_{ij} f_{jk} \mu_{kl}, \quad f_{jk} = \delta_{jk} + \frac{w_k}{w_n}, \quad \mu_{kl} = \left(\frac{\partial \mu_k}{\partial w_l}\right)_{T,P} \quad (i,k,l = 1,2)$$

and δ_{jk} is the Kronecker delta, w_i is the mass fraction of component *i*, $\mathbf{j}_i$ the vector of mass flow of component *i*, $\mathbf{J}_q$ is the vector of reduced heat flow $\mathbf{J}_q = \mathbf{q} - \sum_{i=1}^{n} \mathbf{j}_i h_i$, $\mathbf{q}$ is the total heat flow, h_i is the partial molar enthalpy of species *i*, and ΔH_r is the heat of reaction, ν_i is the stoichiometric coefficient, which is negative for reactants, $H_{ii}^E = (\partial^2 H^E / \partial w_i^2)_{T,P}$, $(i = 1,2)$, and H^E is the excess specific enthalpy or heat of mixing, and the parameters D_{ij} are the diffusion coefficients. The reaction velocity J_r in terms of frequency k_0 and activation energy E for a first order elementary reaction is

$$J_r = k_0 \exp\left(-\frac{E}{RT}\right) \rho_S \tag{4}$$

By using the Fick and Fourier laws in one-dimensional domain of *y*-direction and neglecting any thermodynamic couplings and excess enthalpy effects, Eqs. (1)–(3) become

$$\rho \frac{\partial w_S}{\partial t} = \rho D_S \frac{\partial^2 w_S}{\partial y^2} + \nu_S J_r \tag{5}$$

$$\rho \frac{\partial w_B}{\partial t} = \rho D_B \frac{\partial^2 w_B}{\partial y^2} + \nu_B J_r \tag{6}$$

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial y^2} + (-\Delta H_r) J_r \tag{7}$$

where D_i is the effective diffusivity for component *i*, and *k* the effective thermal conductivity. The initial and boundary conditions with external resistances are

$$t = 0, \quad w_S = w_{So}, \quad w_B = w_{Bo}, \quad T = T_o \tag{8}$$

$$y = \pm L, \quad \rho \frac{\partial w_S}{\partial y} = \frac{k_{gS}}{D_S}(w_{Sb} - w_{Ss}),$$

$$\rho \frac{\partial w_B}{\partial y} = \frac{k_{gB}}{D_B}(w_{Bb} - w_{Bs}), \quad \frac{\partial T}{\partial y} = \frac{h_f}{k}(T_b - T_s) \tag{9}$$