

2008

Thermodynamically Coupled Transport in Simple Catalytic Reactions

Yasar Demirel

University of Nebraska - Lincoln, ydemirel2@unl.edu

Follow this and additional works at: <http://digitalcommons.unl.edu/cbmedemirel>



Part of the [Chemical Engineering Commons](#)

Demirel, Yasar, "Thermodynamically Coupled Transport in Simple Catalytic Reactions" (2008). *Yasar Demirel Publications*. 1.
<http://digitalcommons.unl.edu/cbmedemirel/1>

This Article is brought to you for free and open access by the Chemical and Biomolecular Research Papers -- Faculty Authors Series at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Yasar Demirel Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

INTERNATIONAL JOURNAL OF CHEMICAL
REACTOR ENGINEERING

Volume 6

2008

Article A82

**Thermodynamically Coupled Transport in
Simple Catalytic Reactions**

Yasar Demirel*

*University of Nebraska Lincoln, ydemirel2@unl.edu

ISSN 1542-6580

Copyright ©2008 The Berkeley Electronic Press. All rights reserved.

Thermodynamically Coupled Transport in Simple Catalytic Reactions

Yasar Demirel

Abstract

Considerable work published on chemical reaction-diffusion systems investigates mainly mathematically coupled nonlinear differential equations. This study presents the modeling of a simple elementary chemical reaction with thermodynamically and mathematically coupled heat and mass transport with external mass and heat transfer resistances. 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. The modeling is based on the linear nonequilibrium thermodynamics approach and phenomenological equations by assuming that the system is in the vicinity of global equilibrium. This approach does not need detailed coupling mechanisms. The modeling equations contain the cross coefficients controlling the coupling between heat and mass flows in terms of transport coefficients and surface conditions. These coefficients need to be determined for rigorous analysis of chemical reaction systems with thermodynamically coupled transport phenomena. Some representative numerical solutions of the modeling equations are presented to display the effect of coupling on concentration and temperatures in time and space for simple exothermic catalytic reactions.

KEYWORDS: nonisothermal reaction-diffusion systems, balance equations, external resistances, linear nonequilibrium thermodynamics, thermodynamic coupling, phenomenological equations

1. INTRODUCTION

Considerable work has been published on mathematically coupled chemical reaction-diffusion systems in porous catalyst. Consideration of heat effects due to a chemical reaction, which is either a heat source or a sink, may be necessary for a through analysis of reaction diffusion systems (Aris, 1975; Froment and Bischoff, 1990; Dekker et al., 1995; Demirel and Sandler, 2002; Burghardt and Berezowski, 2003; Demirel, 2006; Xu et al., 2007; Sengers and de Zarate, 2007; de Zarate et al, 2007; Demirel, 2007; Demirel, 2008). Beside that, many catalytic reactions may take place with thermodynamically coupled heat and mass flows, and control the behavior of various physical, chemical, and biological systems (Aono, 1975; Prigogine, 1967; Kondepudi and Prigogine, 1999; Demirel and Sandler, 2001; Gas et al., 2003; Rose and Rose, 2005; Demirel, 2006; Demirel, 2007). 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.

In a previous study, the modeling equations with thermodynamically coupled heat and mass flows without external resistances revealed the cross coefficients controlling the induced heat and mass flows (Demirel, 2006). In a recent study, thermodynamic coupling of a chemical reaction, which is a scalar process, with the vectorial processes of heat and mass flows has been studied (Demirel, 2008). This study presents the modeling equations for thermodynamically and mathematically coupled heat and mass flows with external transport resistances in a catalytic simple chemical reaction. By taking into account external resistances and thermodynamically coupled heat and mass flows, the maximum temperature difference between bulk fluid and catalyst pellet interior is formulated. Such formulations may lead to a comprehensive tool in the study of catalytic reactions in porous catalyst. The modeling is based on the linear nonequilibrium thermodynamics approach and phenomenological equations by assuming that the chemical reaction-diffusion system is in the vicinity of global equilibrium (Demirel and Sandler, 2001; Cukrowski and Kolbus, 2005). The formulations of linear nonequilibrium thermodynamics do not require the detailed mechanism of coupling (Kondepudi and Prigogine, 1999; Caplan and Essig, 1999; Demirel, 2007).

2. BALANCE EQUATIONS

We consider a homogeneous elementary chemical reaction between a substrate (S) and a product (P): $S \rightarrow P$. The well known balance equations are

$$\frac{\partial C_S}{\partial t} = -\nabla \cdot \mathbf{J}_S + \nu_S J_r \quad (1)$$

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{J}_q + (-\Delta H_r) J_r \quad (2)$$

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} is the total heat flow, H_i is the partial molar enthalpy of species i , and ΔH_r is the heat of reaction. Based on the local rate of entropy production equation the linear phenomenological equations for the heat and mass flow vectors are (Demirel, 2006)

$$\mathbf{J}_S = -D_{Se} \nabla C_S - D_{Te} \nabla T \quad (3)$$

$$\mathbf{J}_q = -D_{De} \nabla C_S - k_e \nabla T \quad (4)$$

where D_{Se} is the effective diffusivity for component S, k_e the effective thermal conductivity, and D_{Te} and D_{De} are the effective cross (coupling) coefficients related to thermal diffusion and Dufour effect, respectively. These cross coefficients are discussed in detail elsewhere (Demirel and Sandler, 2001; Demirel, 2007). Reaction velocity is $\frac{dC_S}{\nu_S dt} = J_r$ and the ν_S is the stoichiometric

coefficient, which is negative for reactant ($\nu_S = -1$). Equations (3) and (4) are valid within the vicinity of global equilibrium and obey Onsager's reciprocal relations (Prigogine, 1967; Kondepudi and Prigogine, 1999; Demirel and Sandler, 2001; Demirel 2006). They represent the thermodynamic coupling between the heat and mass flows. The reaction velocity, which is a scalar process, is not coupled with the vectorial flows of heat and mass according to the Curie-Prigogine principle assuming that the reaction-diffusion system takes place in an isotropic medium (Prigogine, 1967; Kondepudi and Prigogine, 1999). A reaction-diffusion system taking place in an anisotropic medium has been discussed elsewhere (Demirel, 2008).

By substituting Eqs. (3) and (4) into Eqs. (1) and (2), and assuming one-dimensional domain of y -direction, as shown in Figure 1, Eqs. (1) and (2) become

$$\frac{\partial C_S}{\partial t} = D_{Se} \frac{\partial^2 C_S}{\partial y^2} + D_{Te} \frac{\partial^2 T}{\partial y^2} + v_S J_r \quad (5)$$

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

The initial and boundary conditions with external mass and heat transfer resistances are (see Figure 1)

$$t = 0 \quad C_S = C_{S0} \quad T = T_0 \quad (7)$$

$$y = \pm L \quad \frac{\partial C_S}{\partial y} = \frac{k_g}{D_{Se}} (C_{Sb} - C_{Ss}) \quad \frac{\partial T}{\partial y} = \frac{h_f}{k_e} (T_b - T_s) \quad (8)$$

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

where k_g is the extra particle mass transfer coefficient, h_f is the heat transfer coefficient, indices b refers to bulk fluid conditions, and L is the half thickness of the slab. Equations (5) to (9) represent the thermodynamically and mathematically coupled, one-dimensional, heat and mass balance equations with external heat and mass transfer resistances. Diffusion may reduce averaged rates relative to that obtained if the concentration was everywhere C_{Ss} . This limitation is quantified as the effectiveness factor (Froment and Bischoff, 1990).

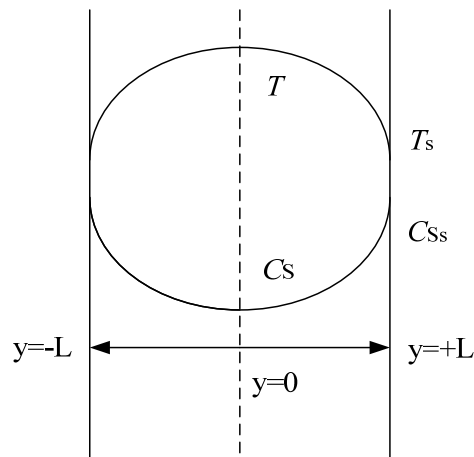


Figure 1: Schematic temperature and concentration profiles in a thin film in a catalyst pellet.

3. TEMPERATURE AND CONCENTRATION GRADIENTS

At steady state, Eqs. (5) and (6) reduces to

$$D_{Se} \frac{\partial^2 C_S}{\partial y^2} + D_{Te} \frac{\partial^2 T}{\partial y^2} = J_r \quad (10)$$

$$-\left(D_{De} \frac{\partial^2 C_S}{\partial y^2} + k_e \frac{\partial^2 T}{\partial y^2} \right) = (-\Delta H_r) J_r \quad (11)$$

By eliminating of the reaction terms in Eqs. (10) and (11) and integrating once from pellet center ($L = 0$) to surface with the boundary conditions, we obtain

$$\begin{aligned} & \left(D_{Se} + \frac{D_{Te}}{(-\Delta H_r)} \right) \frac{dC_S}{dy} \Big|_L + \left(D_{De} + \frac{k_e}{(-\Delta H_r)} \right) \frac{dT}{dy} \Big|_L = 0 \\ & = \left(D_{Se} + \frac{D_{Te}}{(-\Delta H_r)} \right) \frac{k_g}{D_{Se}} (C_{Sb} - C_{Ss}) + \left(D_{De} + \frac{k_e}{(-\Delta H_r)} \right) \frac{h_f}{k_e} (T_b - T_s) \end{aligned} \quad (12)$$

From the right hand side of Eq. (12), we have the temperature difference between surface and bulk fluid conditions ($T_s - T_b$)

$$T_s - T_b = \left(\frac{D_{Se}(-\Delta H_r) + D_{De}}{D_{Te}(-\Delta H_r) + k_e} \right) \frac{Sh}{Nu} (C_{Sb} - C_S) \quad (13)$$

where Sh and Nu are the Sherwood and Nusselt numbers, respectively

$$Sh = \frac{k_g L}{D_{Se}}, \quad Nu = \frac{h_f L}{k_e} \quad (14)$$

After the second integration from pellet center to surface and some arrangements, the total temperature difference between the interior of pellet and bulk fluid ($T - T_b$) becomes

$$T - T_b = \left(\frac{D_{Se}(-\Delta H_r) + D_{De}}{D_{Te}(-\Delta H_r) + k_e} \right) (C_{Ss} - C_S) + (T_s - T_b) \quad (15)$$

The first term of the right hand side of Eq. (15) represents the internal temperature difference, while the second term is the external temperature difference. After substituting Eq. (13) into Eq. (15) to eliminate the external temperature difference ($T_s - T_b$), we find the maximum temperature difference between bulk fluid and catalyst pellet interior ($T - T_b$)

$$T - T_b = \left(\frac{D_{Se}(-\Delta H_r) + D_{De}}{D_{Te}(-\Delta H_r) + k_e} \right) \left[(C_{Ss} - C_S) + \frac{\text{Sh}}{\text{Nu}} (C_{Sb} - C_{Ss}) \right] \quad (16)$$

By multiplying the both side of Eq. (16) by (C_{Ss}/T_s) and after arranging, we have the dimensionless temperature ϕ and concentration of reactant S θ_S , which are interrelated at steady state by the following equations

$$\phi = \beta'_s (1 - \theta_S) + \beta'_s \frac{\text{Sh}}{\text{Nu}} (\theta_{Sb} - 1) + \phi_b \quad (17)$$

$$\theta_S = 1 + \frac{\text{Sh}}{\text{Nu}} (\theta_{Sb} - 1) - \frac{(\phi - \phi_b)}{\beta'_s} \quad (18)$$

where

$$\theta_S = \frac{C_S}{C_{Ss}}, \quad \phi = \frac{T}{T_s}, \quad \theta_{Sb} = \frac{C_{Sb}}{C_{Ss}}, \quad \phi_b = \frac{T_b}{T_s}, \quad \beta'_s = \left(\frac{D_{Se}(-\Delta H_r) + D_{De}}{D_{Te}(-\Delta H_r) + k_e} \right) \frac{C_{Ss}}{T_s}$$

The maximum temperature difference occurs when $C_S = 0$, and after multiplying both sides with (C_{Sb}/T_b) Eq. (16) becomes

$$\frac{T_{\max} - T_b}{T_b} = \frac{\beta'_b}{\theta_{Sb}} \left[1 - \frac{\text{Sh}}{\text{Nu}} (1 - \theta_{Sb}) \right] \quad (19)$$

where

$$\beta'_b = \left(\frac{D_{Se}(-\Delta H_r) + D_{De}}{D_{Te}(-\Delta H_r) + k_e} \right) \frac{C_{Sb}}{T_b} \quad (\text{Based on the bulk fluid conditions})$$

The value of β'_b is a measure of nonisothermal effect at bulk fluid conditions. Eq. (19) shows the effects of the coupling and external resistances on the maximum temperature difference in a catalyst pellet; it reduces to a similar equation at surface conditions when there is no coupling between heat and mass flows (Froment and Bischoff, 1990; Tavera 2005).

4. MODELING EQUATIONS

The reaction velocity J_r in terms of frequency k_0 and activation energy E for the first order elementary reaction is

$$J_r = -k_v C_S = -k_0 \exp\left(\frac{-E}{RT}\right) C_S \quad (20)$$

By substituting Eq. (20) into Eqs. (5) and (6), we may describe the thermodynamically and mathematically coupled heat and mass flows in a nonisothermal chemical reaction-diffusion system

$$\frac{\partial C_S}{\partial t} = D_{Se} \nabla^2 C_S + D_{Te} \nabla^2 T - k_0 \exp\left(\frac{-E}{RT}\right) C_S \quad (21)$$

$$\rho C_p \frac{\partial T}{\partial t} = D_{De} \nabla^2 C_S + k_e \nabla^2 T + (-\Delta H_r) k_0 \exp\left(\frac{-E}{RT}\right) C_S \quad (22)$$

Here the transport coefficients D_{Se} , D_{Te} , D_{De} , and k_e may have tensorial properties depending on the medium in which the transport takes place.

For a one-dimensional transport in a simple slab, Eqs. (21) and (22) reduce to the following dimensionless forms

$$\frac{\partial \theta_S}{\partial \tau} = \frac{\partial^2 \theta_S}{\partial z^2} + \varepsilon \frac{\partial^2 \phi}{\partial z^2} - \text{Da}_S \theta_S \exp\left[\gamma \left(1 - \frac{1}{\phi}\right)\right] \quad (23)$$

$$\frac{1}{\text{Le}} \frac{\partial \phi}{\partial \tau} = \frac{\partial^2 \phi}{\partial z^2} + \omega \frac{\partial^2 \theta_S}{\partial z^2} + \text{Da}_S \beta'_s \theta_S \exp\left[\gamma \left(1 - \frac{1}{\phi}\right)\right] \quad (24)$$

where

$$z = \frac{y}{L}, \quad \tau = \frac{D_{Se} t}{L^2}, \quad \text{Da}_S = \frac{L^2 k_0 \exp(-E/RT_s)}{D_{Se}}, \quad \gamma = \frac{E}{RT_s}, \quad \text{Le} = \frac{k_e / \rho C_p}{D_{Te}} = \frac{\alpha_e}{D_{Te}}$$

$$\varepsilon = \frac{D_{Te} T_s}{D_{Se} C_{Ss}}, \quad \omega = \frac{D_{De} C_{Ss}}{k_e T_s}$$

$$\beta'_s = \frac{[D_{Se}(-\Delta H_r) + D_{De}] C_{Ss}}{[k_e + D_{Te}(-\Delta H_r)] T_s} \quad (\text{Based on surface conditions})$$

The initial and boundary conditions become

$$\begin{aligned}
\tau = 0 & \quad \theta_S = \theta_{S_0} \quad \phi = \phi_0 \\
z = \pm 1, \tau > 0 & \quad \frac{\partial \theta_S}{\partial z} = \text{Sh}(\theta_{Sb} - 1), \quad \frac{\partial \phi}{\partial z} = \text{Nu}(\phi_b - 1) \\
z = 0, \tau > 0 & \quad \frac{\partial \theta_S}{\partial z} = \frac{\partial \phi}{\partial z} = 0
\end{aligned} \tag{25}$$

Da_S is the Damköhler number, and measures the intrinsic rate of the reaction relative to that of the diffusions. For an exothermic reaction $\beta'_s > 0$ and as the value of β'_s approaches zero, system becomes isothermal. The coefficients ε and ω above are associated with the cross coefficients, and hence control the coupled phenomena between the mass and heat flows in the y -direction. The coefficients ε and ω are related to measurable effective transport coefficients and surface temperature and pressure. The coefficient ε depends on effective thermal diffusivity, while ω depends on effective Dufour effect. Therefore, Eqs. (23) to (25) account the induced effects, which may contribute towards multiple states and diversified behavior of chemical reaction-diffusion systems under some specific hydrodynamic and kinetic conditions (Kondepudi and Prigogine, 1999; Demirel, 2007).

At steady state, Eqs. (23) and (24) reduces to

$$0 = \frac{\partial^2 \theta_S}{\partial z^2} + \varepsilon \frac{\partial^2 \phi}{\partial z^2} - \text{Da}_S \theta_S \exp \left[\gamma \left(1 - \frac{1}{\phi} \right) \right] \tag{26}$$

$$0 = \frac{\partial^2 \phi}{\partial z^2} + \omega \frac{\partial^2 \theta_S}{\partial z^2} + \text{Da}_S \beta'_s \theta_S \exp \left[\gamma \left(1 - \frac{1}{\phi} \right) \right] \tag{27}$$

By substituting Eq. (17) into Eq. (26), we have

$$\frac{d^2 \theta_S}{dz^2} = \frac{\text{Da}_S \theta_S}{(1 - \varepsilon \beta'_s)} \exp \left[\gamma \left(1 - \left\{ \beta'_s \left((1 - \theta_S) + \frac{\text{Sh}}{\text{Nu}} (\theta_{Sb} - 1) \right) + \phi_b \right\}^{-1} \right) \right] \tag{28}$$

This nonlinear ordinary differential equation with the boundary conditions in Eq. (25) describes the change of concentration in space at steady state when the heat and mass flows are thermodynamically coupled. A similar ordinary differential equation for ϕ can be derived by substituting Eq. (18) into Eq. (27).

5. RESULTS

Table 1 lists the parameters used in the representative solutions for the following exothermic reaction systems: (1) the synthesis of higher alcohols from carbon monoxide and hydrogen with $\beta' = 0.00085$, and (2) the hydrogenation of benzene with $\beta' = 0.12$. The parameters chosen for Sh, Nu, θ_b , and ϕ_b satisfy Eq. (19). The heat effect for the first system should be small because of the value of low β' . Both the systems consist of relatively slow chemical reactions as $Da_s = 0.5$.

Table 1. Experimental (Hlavacek et al., 1969, Froment and Bischoff, 1999) and assumed values of parameters for the two exothermic industrial reaction systems used in the representative solutions of Eqs. (23) and (24)

Reaction systems	Da_s^*	$\beta_b' \approx \beta_s'$	γ	Le	Sh ^{'*}	Nu ^{'*}	θ_{sb}	ϕ_b^*	ϕ_{max} Eq. (19)
1	0.5*	0.00085	28.4	0.0002	5.0	0.05	1.1	0.995	1.0034
2	0.5	0.12	15.0	0.006	2.0	0.2	1.1	0.970	1.1816

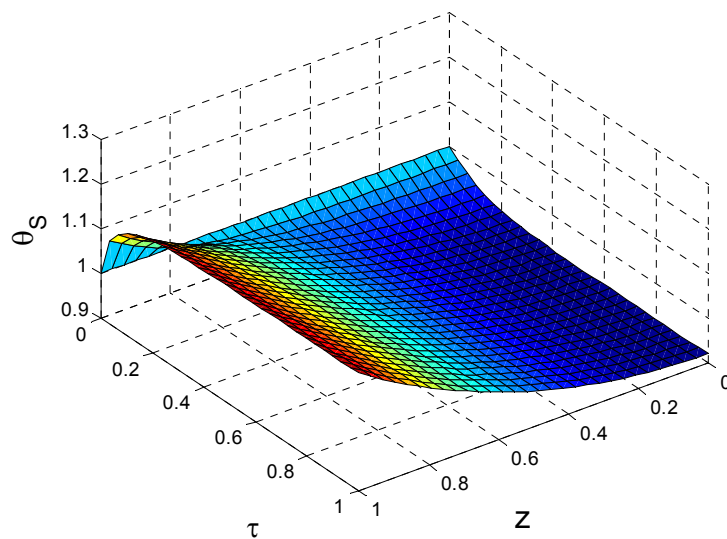
1. Synthesis of higher alcohols from CO and H₂

2. Hydrogenation of benzene

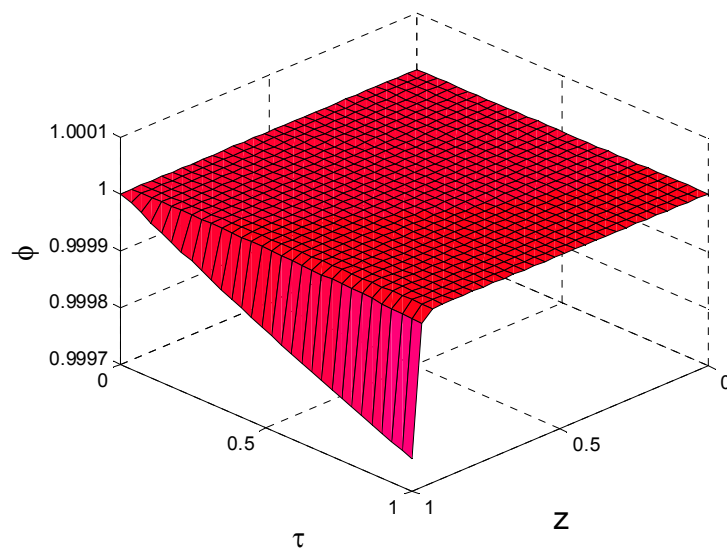
* Assumed values

Approximate representative solutions of Eqs. (23) and (24) with the initial and boundary conditions are obtained from MATLAB partial differential equation solver. Accuracy of these solutions depends on the reliable effective transport coefficients and cross coefficients ϵ and ω . The solutions are based on the assumptions that the chemical reaction-diffusion system takes place in an isotropic medium and no thermodynamic coupling occurs between the transport processes and chemical reaction.

Figure 2 displays the dynamic behavior of dimensionless concentrations and temperatures in time and space with $\omega = 0.05$ and $\epsilon = 0.05$, while Figure 3 displays them with $\omega = 0.0$ and $\epsilon = 0.0$ for the first system. Hence, Figures 2 and 3 display the results with and without thermodynamic coupling, respectively. The results displayed in Figures 2 and 3 show small increase in temperatures due to coupling, although $\beta' = 0.00085$, which suggests that the reaction is close to isothermal. Figures 4 and 5 display the dimensionless concentrations and temperatures at $\tau = 1$ with and without thermodynamic coupling, respectively. They, also display the sharp changes in temperatures close to the surface of pellet. The temperature remains uniform until the vicinity of surface of pellet at around $z = 0.9$.

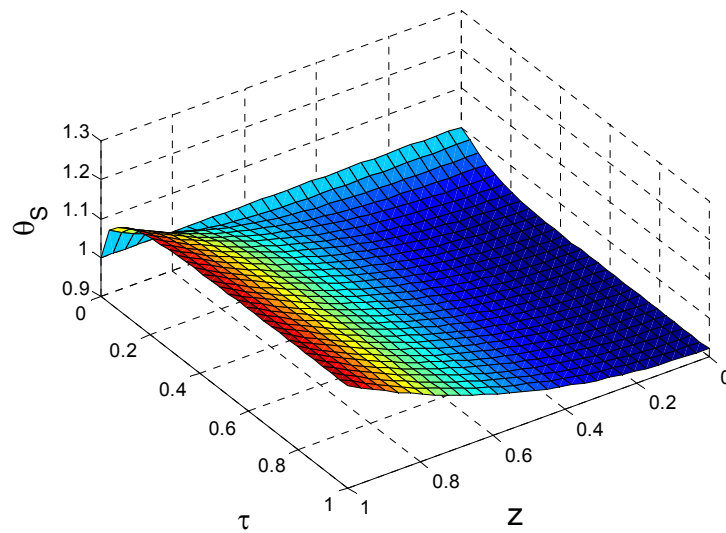


(a)

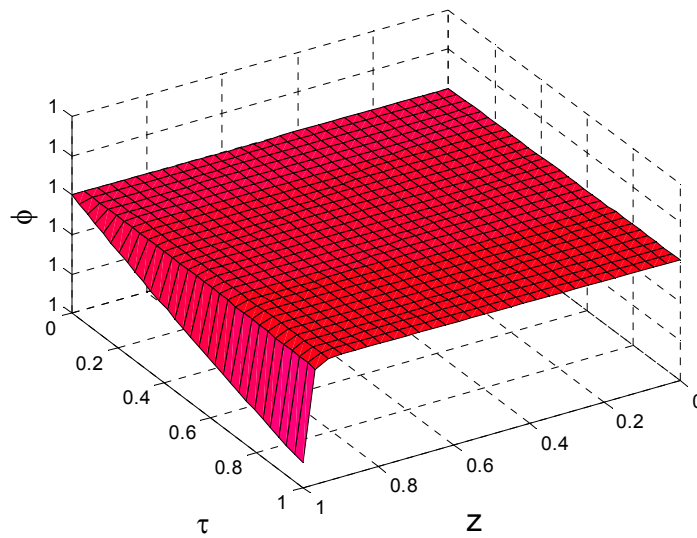


(b)

Figure 2: Synthesis of higher alcohols from CO and H₂ with $\varepsilon = 0.05$ and $\omega = 0.05$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations in time and space, (b) dimensionless temperatures in time and space.



(a)



(b)

Figure 3: Synthesis of higher alcohols from CO and H₂ with $\varepsilon = 0.0$ and $\omega = 0.0$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations in time and space, (b) dimensionless temperatures in time and space.

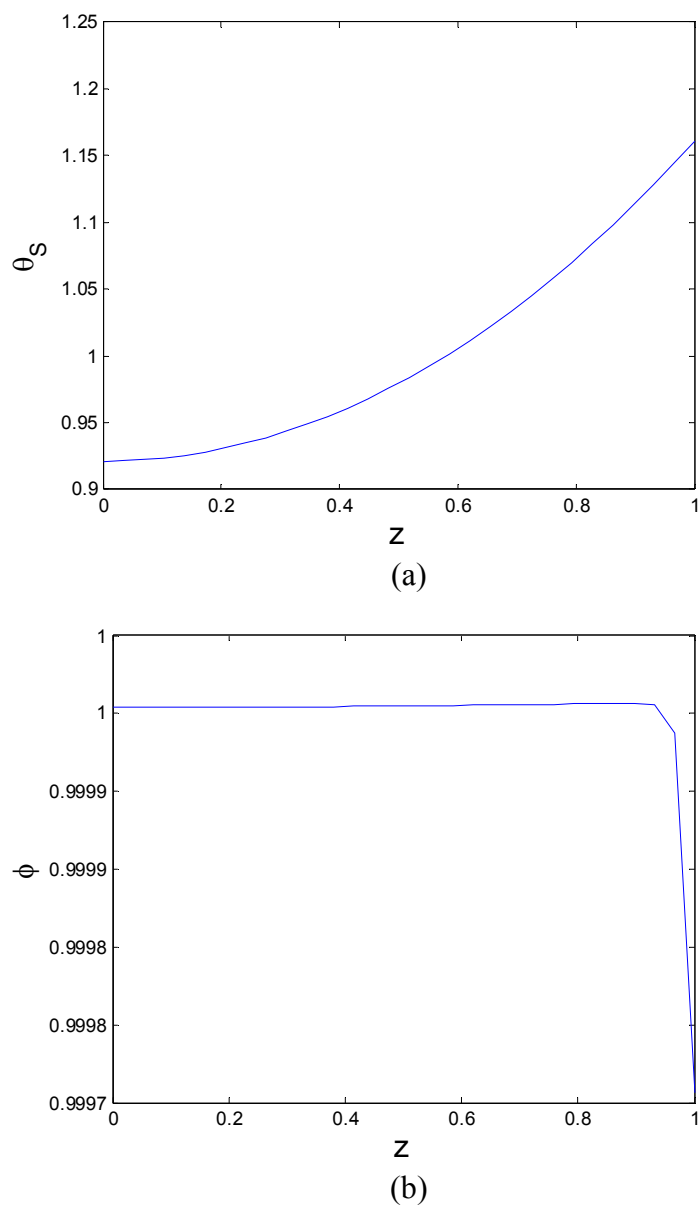


Figure 4: Synthesis of higher alcohols from CO and H₂ with $\varepsilon = 0.05$ and $\omega = 0.05$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations at $\tau = 1$, (b) change of dimensionless temperatures at $\tau = 1$.

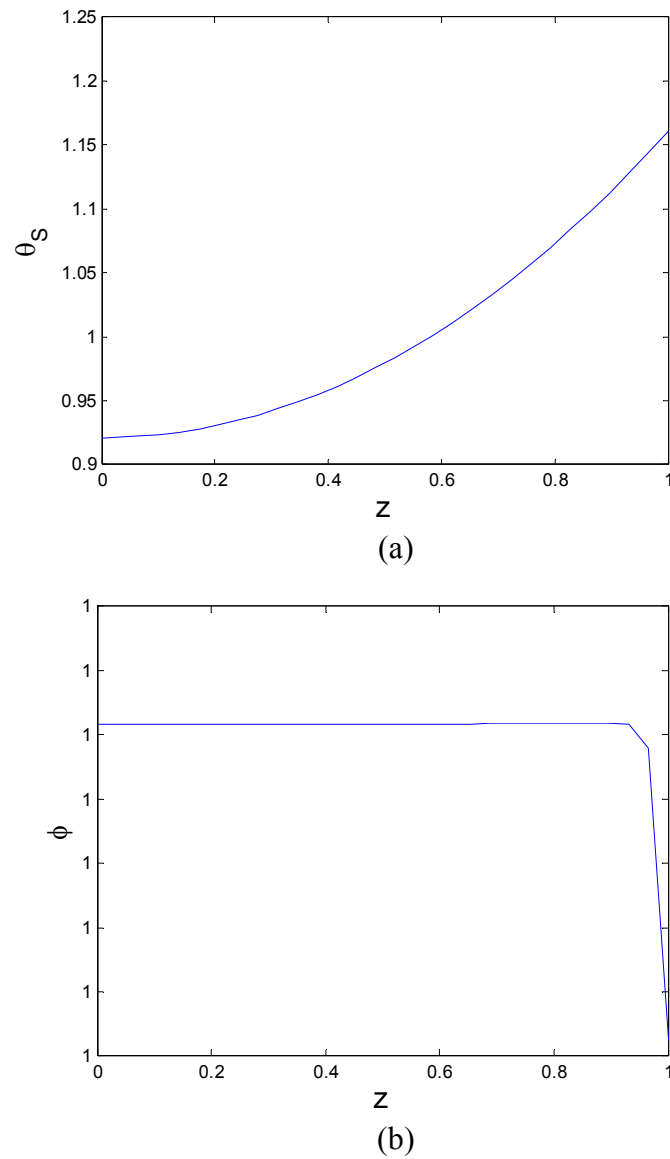


Figure 5: Synthesis of higher alcohols from CO and H₂ with $\varepsilon = 0.0$ and $\omega = 0.0$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations at $\tau = 1$, (b) change of dimensionless temperatures at $\tau = 1$.

For the hydrogenation of benzene, Figures 6 and 7 display the coupled and uncoupled dimensionless concentration and temperature changes in time and space. The effects of coupling on the concentration and temperature are more apparent for the second system with $\beta' = 0.12$.

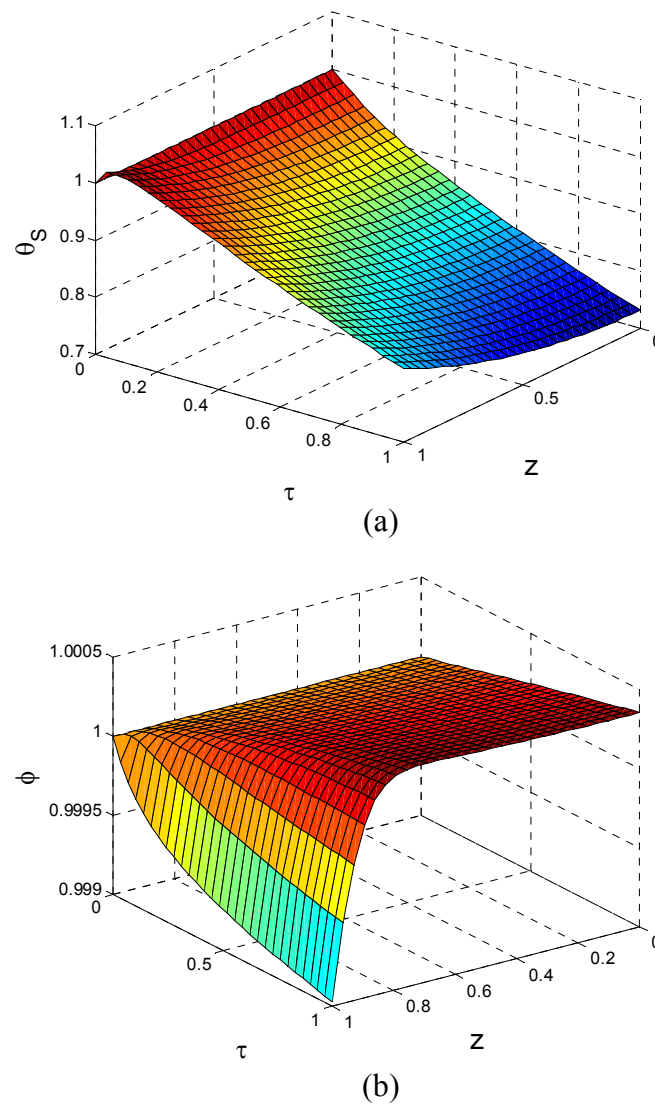
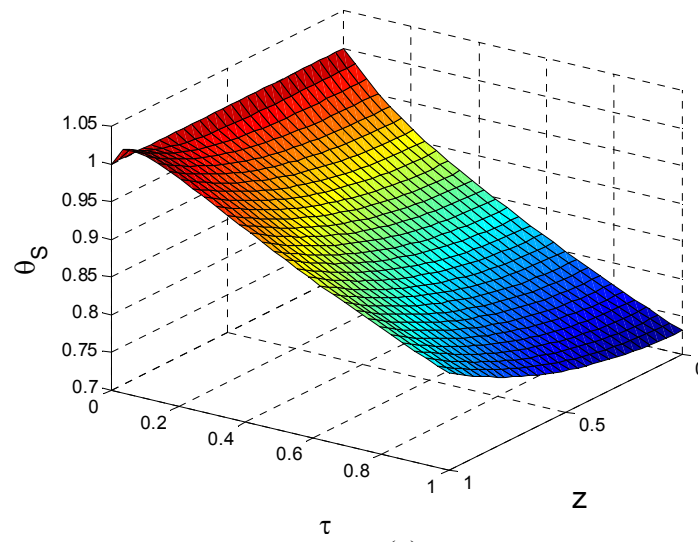
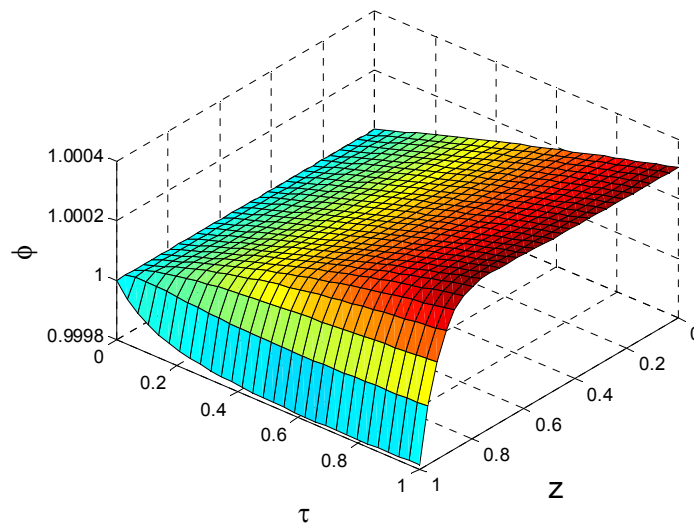


Figure 6: Hydrogenation of benzene with $\varepsilon = 0.05$ and $\omega = 0.05$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations in time and space, (b) dimensionless temperatures in time and space.



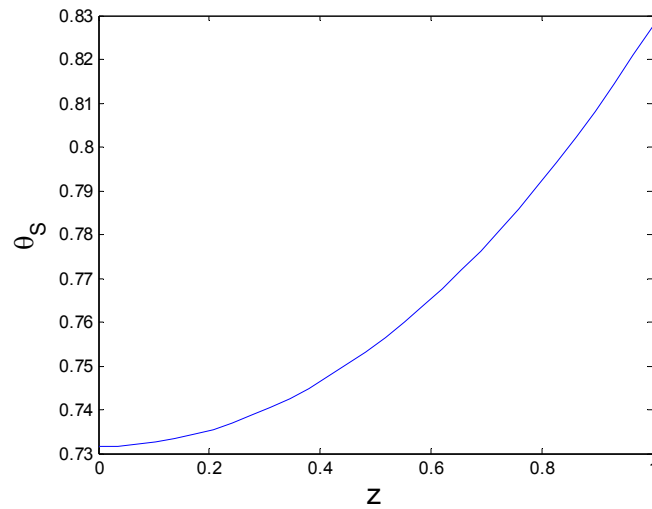
(a)



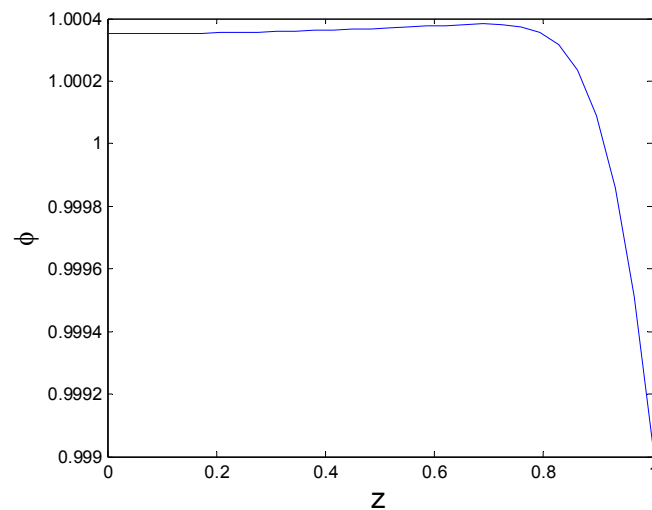
(b)

Figure 7: Hydrogenation of benzene with $\varepsilon = 0.0$ and $\omega = 0.0$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations in time and space, (b) dimensionless temperatures in time and space.

For the second reaction system, Figures 8 and 9 display the dimensionless concentrations and temperatures at $\tau = 1$ with and without thermodynamic coupling, respectively. The value of ϕ remains uniform until $z = 0.8$, after which it drops sharply.

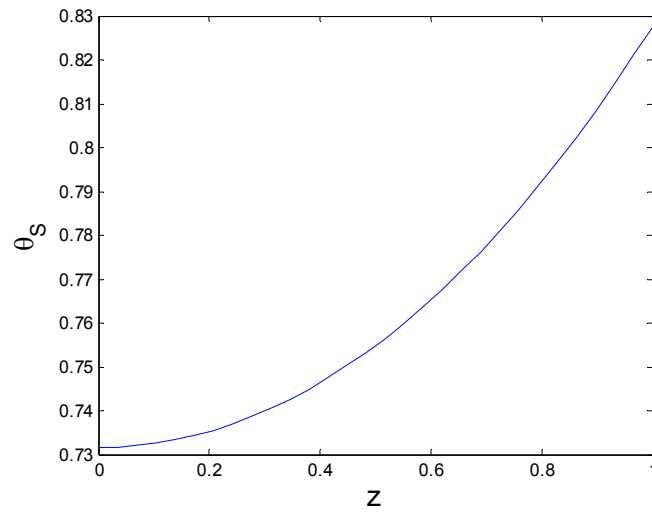


(a)

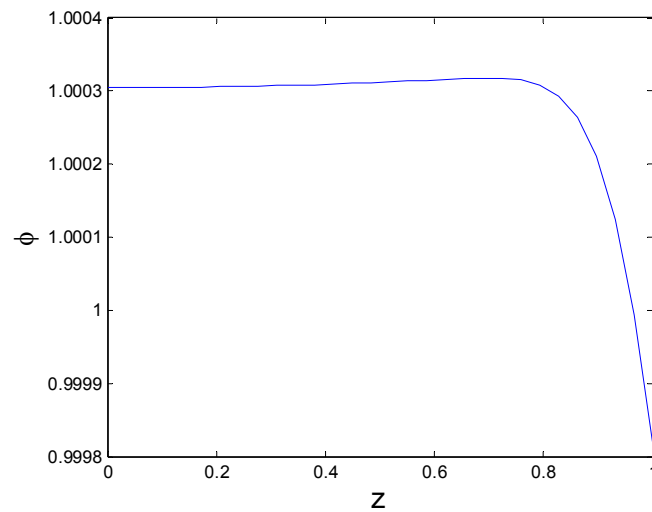


(b)

Figure 8: Hydrogenation of benzene with $\varepsilon = 0.05$ and $\omega = 0.05$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations at $\tau = 1$, (b) change of dimensionless temperatures at $\tau = 1$.



(a)



(b)

Figure 9: Hydrogenation of benzene with $\varepsilon = 0.0$ and $\omega = 0.0$, and the other parameters listed in Table 1: (a) change of dimensionless concentrations at $\tau = 1$, (b) change of dimensionless temperatures at $\tau = 1$.

6. CONCLUSIONS

The balance equations are derived for thermodynamically and mathematically coupled system of heat and mass flows for simple catalytic reaction systems. No thermodynamic coupling takes place between chemical reaction and transport processes. The maximum temperature difference between the bulk phase and center of a pellet is also formulated with the effects of coupling as well as external mass and heat transfer resistances. These modeling equations are based on the linear nonequilibrium thermodynamics approach and phenomenological equations, and define some unique cross coefficients controlling the induced flows of heat and mass due to thermodynamic couplings. The modeling equations can describe the change of concentration and temperature in time and space for a simple reaction system with thermodynamically coupled heat and mass flows and with external resistances. Taking into account the thermodynamic coupling, heat effects, and external resistances would lead to comprehensive and rigorous tools for describing chemical reaction-diffusion systems.

NOTATION

C_{Ss}	reactant concentration at surface, mol m ⁻³
Da	Damköhler number
D_{Se}	effective diffusion coefficient for the substrate S, m ² s ⁻¹
D_{De}	coupling coefficient related to the Dufour effect, J m ² mol ⁻¹ s ⁻¹
D_{Te}	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, mol m ⁻² s ⁻¹
J_q	conduction heat flux W m ⁻²
J_r	reaction rate (velocity) 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	Lewis number
Nu	Nusselt number
Sh	Sherwood number
t	time, s ⁻¹
T	temperature, K
z	dimensionless distance

Greek letters

α_e	effective thermal diffusivity m ² s ⁻¹
------------	--

β	thermicity group, dimensionless
β'	thermicity group for coupled heat and mass flows, dimensionless
ε	dimensionless parameter related to Soret effect (thermal diffusion)
γ	Arrhenius group, dimensionless
ϕ	dimensionless temperature
θ	dimensionless concentration
ρ	density, kg m^{-3}
τ	dimensionless time
ω	dimensionless parameter related to Dufour effect

Subscripts

b	bulk fluid
D	Dufour
e	effective
q	heat
r	reaction
s	surface
T	thermal diffusivity

REFERENCES

Aris, R., "The mathematical theory of diffusion and reaction in permeable catalysts. Volume 1. The theory of the steady state", Clarendon Press, Oxford, 1975.

Aono, O., "Thermodynamic coupling of diffusion with chemical reaction", *J. Stat. Phys.*, 13, 331-335, 1975.

Caplan, R.S., Essig, A., "Bioenergetics and Linear Nonequilibrium Thermodynamics. The Steady State", reprint, Harvard University Press, New York, 1999.

Cukrowski, A.S., Kolbus. A., "On validity of linear phenomenological nonequilibrium thermodynamics equations in chemical kinetics", *Acta Physica Polonica B.*, 36, 1485-1507, 2005.

De Zarate, J.M.O., Sengers, J.V., Bedeaux, D., Kjelstrup, S., "Concentration fluctuations in non-isothermal reaction-diffusion systems", *J. Chem. Phys.*, 127, No: 034501, 2007.

Dekker, F.H.M., Blik, A., Kapteijn, F., Moulijn, “Analysis of mass and heat transfer in transient experiments over heterogeneous catalyst”, *Chem. Eng. Sci.*, 50, 3573-3580, 1995.

Demirel, Y., Sandler, S.I., “Linear non-equilibrium thermodynamics theory for coupled heat and mass transport”, *Int. J. Heat Mass Transfer*, 44, 2439-2451, 2001.

Demirel, Y., Sandler, S.I., “Effects of concentration and temperature on the coupled heat and mass transport in liquid mixtures”, *Int. J. Heat Mass Transfer*, 45, 75-86, 2002.

Demirel, Y., “Non-isothermal reaction diffusion system with thermodynamically coupled heat and mass transfer”, *Chem. Eng. Sci.*, 61, 3379-3385, 2006.

Demirel, Y., “Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical, Chemical and Biological Systems”, 2nd ed., Elsevier, Amsterdam, 2007.

Demirel, Y., “Modeling of thermodynamically coupled reaction-transport systems”, *Chem. Eng. J.*, 139, 106-117, 2008.

Froment, F.G., Bischoff, K.B., “Chemical Reactor Analysis and Design”, Wiley, New York, 1999.

Gas, P., Girardeaux, C., Mangelinck, D., Portavoce, A., “Reaction and diffusion at interfaces of micro- and nanostructured materials”, *Mat. Sci. Eng. B*, 101, 43-48, 2003.

Hlavecek, H., Kubicek, M., Marek, M., “Analysis of nonstationary heat and mass transfer in a porous catalyst particle I”, *J. Catalysis*, 15, 31-42, 1969.

Kondepudi, D., Prigogine, I., “Modern Thermodynamics; From Heat Engines to Dissipative Structures”, Wiley, New York, 1999.

Prigogine, I., “Introduction to Thermodynamics of Irreversible Processes”, 3rd ed. Wiley, New York, 1967.

Rose, W., Rose, D., “An up grade porous medium coupled transport process algorithm”, *Trans. Porous Med.*, 59, 357-372, 2005.

Sengers, J.V., de Zarate, J.M.O., “Thermal fluctuations in non-equilibrium thermodynamics”, *J Non-Equilibrium Thermodynamics*, 32, 319-329, 2007.

Tavera, E.M., “Analytical expression for the effectiveness factor: the nth-order reaction in a slab geometry”, *Chem. Eng. Sci.*, 60, 907-916, 2005.

Xu, J., Kjelstrup, S., Bedeaux D., Simon, J-M., “Transport properties of $2F = F_2$ in a temperature gradient as studied by molecular dynamics simulations”, *Phys. Chem. Chem. Phys.*, 9, 969–981, 2007.