A thermodynamic approach to the passive boundary control of tubular reactors

N. Ha Hoang∗,∗∗ Denis Dochain∗∗

∗ Faculty of Chemical Engineering, University of Technology, VNU-HCM, 268 Ly Thuong Kiet Str., Dist. 10, HCM City, Vietnam
∗∗ CESAME, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium (e-mails: {ha.hoang,denis.dochain}@uclouvain.be)

Abstract: This paper proposes a thermodynamics based approach for the boundary control of distributed single phase reactive systems in one spatial dimension. More precisely, this approach is motivated by the so-called thermodynamic availability directly derived from the concavity of the entropy function for homogeneous mixtures. On this basis, a general connection to the boundary control is developed for the case of tubular reactors by selecting an appropriate input-output pair. In this control framework, we shall show that to be (strictly) passive, a necessary and sufficient condition for the dissipation that is strongly related to the transport phenomena and chemical reaction has to be fulfilled. Consequently, a proportional boundary feedback control law globally stabilizes the reactor at a desired stationary profile. For a simple study without convection, the dissipation condition holds thanks to the irreversible entropy production.

Keywords: tubular reactors, passivity, irreversible thermodynamics, transport phenomena.

1. INTRODUCTION

This paper deals with the extension of the passivity theory (Willems (1972); Van Der Schaft (2000); Maschke et al. (2000); Brogliato et al. (2007)) of finite dimensional (FD) systems

2

to the important case of tubular chemical reactors using thermodynamic foundations (Keenan (1951); Glansdorff and Prigogine (1964); Ydstie and Alonso (1997); Ruszkowski et al. (2005); Hoang et al. (2012)). This benchmark case study indeed belongs to infinite dimensional - distributed parameter (IFD-DP) systems described generally by Partial Differential Equations (PDE) models and so far, its nonlinear dynamics is naturally distributed in space with the presence of transport phenomena such as convection, diffusion and possibly conduction together with chemical reaction (De Groot and Mazur (1962)). Similarly to the lumped parameter case described by ODEs (for instance the CSTR models (Hoang et al. (2012))), the DP reaction systems may also exhibit multiple (stable or unstable) stationary profiles (Gawdzik and Berezowski (1987)). Consequently, the stabilization of the DP reaction systems represents interesting challenging difficulties from a control point of view.

The controller design for the DP systems has broadly studied in literature (Ray (1978); Ruszkowski et al. (2005) and references therein). A simple approach is to discretize spatially the original PDEs using finite difference approximations, finite volume or Galerkin’s methods (Quarteroni and Valli (1996)). This dimension reduction step that is also known as early lumping (Ray (1978)) results in a FD system. Controllers are then synthesized based on the resulting set of ODEs by means of differential geometry or Lyapunov theory (Khallil (2002)) or more general passive techniques (Van Der Schaft (2000); Brogliato et al. (2007)). Yet designing the controller on the original PDE model allows us to better account for the intrinsic distributed parameter dimension of the system. Such an approach is often referred as late lumping (Ray (1978)).

In this work, we consider the control of the tubular reactors using the late lumping approach on the basis of physical considerations (Keenan (1951); Glansdorff and Prigogine (1964); Dammers and Tels (1974); Tarbell (1977); Georgakis (1986); Ydstie and Alonso (1997); Hangos et al. (1999); Favache and Dochain (2009); Ederer et al. (2011)). In particular, the thermodynamic availability concept has been extensively used in (Alonso and Ydstie (2001); Ruszkowski et al. (2005); Antelo et al. (2007)) for the stabilization of transport reaction systems. The mentioned results are of great interest, yet for instance limited to zeroth order reaction or isothermal/adiabatic transformations (Alonso and Ydstie (2001)). In (Ruszkowski et al. (2005)), the authors combined the thermodynamic availability with the inventory based control strategy to stabilize isothermal tubular reactors. On the basis of our previous works (Hoang et al. (2011, 2012)), we show in this paper that the availability can be extended with less restrictive conditions and can also be considered as a storage function of the passivity theory. In this framework, the boundary control of non isothermal tubular reactors

1 This paper presents research results of the Belgian Network DYSCO (Dynamical Systems, Control and Optimization), funded by the Interuniversity Attraction Poles Programme, initiated by the Belgian State, Science Policy Office. The authors also gratefully acknowledge the support of the FNRS. The scientific responsibility rests with its authors.

2 Their dynamics are described by Ordinary Differential Equations (ODE).
around a desired stationary state will be formulated and studied.

The paper is organized as follows. Section 2 is dedicated to thermodynamic foundations required for the present work, including the definition of the availability function and its properties. The thermodynamically consistent modeling of reaction systems is also introduced in this section. Section 3 concentrates on the study of the tubular reactors. The boundary control problem is then derived and treated in the framework of passivity theory.

Notations: The following notations are considered throughout this paper:

- $V$ and $\Omega$ are the volume and surrounding surface of the real physical system embedded in a Cartesian coordinate system $\mathbb{R}^l$, $l = 1, 2, 3$.
- $\langle e, v \rangle_\Omega$ is the inner product of two vector valued functions $e$ and $v$ defined on $\Omega$:
  \[ \langle e, v \rangle_\Omega = \int_\Omega e \cdot v \ d\Omega \]
  where $\langle e, v \rangle = e^T v$ and $\|e\|^2 = \langle e, e \rangle$.

2. TOWARDS NON EQUILIBRIUM THERMODYNAMICS OF OPEN SYSTEMS

In this work, the non-equilibrium thermodynamics is central for deriving a candidate storage function usable for the control purpose of open systems within the framework of the passivity theory. In this section, we first recall some thermodynamic concepts. On this basis, the definition of the thermodynamic availability is represented and its properties are given. Due to the natural positivity, this function is considered as a candidate Lyapunov function for the boundary control problem of distributed parameter homogeneous reaction systems.

The following hypotheses are used throughout the paper:

(\text{Hp1}) The reaction mixture is incompressible.
(\text{Hp2}) The chemical transformation taking place in the system is under isobaric conditions.

2.1 Thermodynamic foundations

In chemical engineering, equilibrium thermodynamics plays a key role and provides useful guidelines for studying the behaviour of the system dynamics when any spontaneous transformation occurs (Glaeseroff and Prigogine (1964); Callen (1985)). The variables considered in equilibrium thermodynamics are split into the extensive variables (such as the internal energy $U$, the volume $V$ and the mass $m_k$ of each species) and intensive ones (such as the temperature $T$, the pressure $p$ and the chemical potential $\mu_k$) (Callen (1985)). Note that the extensive variables depend on the "size" of the overall system whereas the intensive variables are defined at every location within the system. The fundamental relation of thermodynamics expresses the entropy $S$ of a given phase as a function of the extensive variables via the Gibbs equation (Callen (1985)). The compact form of the Gibbs equation under hypothesis (\text{Hp2}) is written as follows:

\[ dS = w^T dZ \]  

(1)

with:

\[ w = \left( \frac{1}{T}, -\frac{\mu_k}{T} \right)^T, \quad Z = (H, m_k)^T \]  

(2)

where $H = U + pV$ is the enthalpy. Since the entropy $S$ is also an extensive variable, it is an homogeneous function of degree 1 with respect to $Z$. From Euler’s theorem we get (Callen (1985)):

\[ S(Z) = w^T Z \]  

(3)

With the help of (1), the variation of the entropy defined in (3) leads to the following equation:

\[ dw^T Z = 0 \]  

(4)

which is also a well known form of the so-called Gibb-Duhem relation.

(1)(3)(4) hold when the states of the system presented by $Z$ and $w$ in (2) are well-defined (e.g. in thermodynamic equilibrium). It is worth noting that the states of the open system are generally non-equilibrium states due to the changes with the surrounding medium, and in particular only its steady states can be equilibrium ones when the appropriate boundary conditions which are really imposed on the system are justified (De Groot and Mazur (1962)).

Thanks to the Hypothesis of Local Equilibrium (HLE), it is therefore possible to describe open systems on the basis of the equilibrium thermodynamics. HLE states that the local equilibrium state is assumed to be well-defined in the infinitesimal element $dV$ and the present state can be characterized by the same variables as at equilibrium and is independent of the rate of evolution (De Groot and Mazur (1962)). In this case, all macroscopic extensive variables are represented throughout their (mass) density quantities and defined as follows:

\[ S = \int_V \rho s \ dV \]  

(5)

and

\[ Z = \int_V \rho z \ dV \]  

(6)

with,

\[ z = (h, \omega_k)^T \]  

(7)

In (5)(6), $\rho$ is the total mass density; $\omega_k$ denotes for the mass fraction; $s$ and $h$ are the entropy and enthalpy densities, respectively. As a consequence of the HLE, (1)(3)(4) can also be applied for open systems and in this case, they are rewritten using the density quantities as follows:

\[ ds = w^T dz \]  

(8)

and

\[ s(z) = w^T z \]  

(9)

\[ dw^T z = 0 \]  

(10)

In particular, in thermodynamics the intensive variables $w$ can be viewed as the gradient of the entropy $s(z)$ (9). From the mathematical point of view, we have:

\[ w(z) = \frac{\partial s(z)}{\partial z} \]  

(11)

The dynamical behaviour of open systems is given by considering only the energy and material balance equations of the variable $z$ defined in (7). Additionally, the balance equation for the entropy $s$ (9) can be deduced from the balance equations of the variable $z$ using the (local) Gibbs
equation given in (8). The use of the entropy balance gives knowledge on the evolution of the system. Indeed, this balance is not conservative: there exists a source term \( \Sigma_s \) which is always positive (due to the second law of thermodynamics) so that (De Groot and Mazur (1962)):

\[
\frac{\partial \rho s}{\partial t} = \frac{\partial J_{s, tot}}{\partial x} + \Sigma_s \quad (12)
\]

where \( J_{s, tot} \) is the total entropy exchange flux. The positive definiteness of the irreversible entropy production \( \Sigma_s \) defined in (12) holds for any evolution. We refer the reader to Appendix A for a further investigation on this issue.

The open thermodynamic system defined by (8)-(10) together with (12) on the basis of the balance equations of \( z \) is called the thermodynamically consistent model (Glansdorff and Prigogine (1964); Hoang and Dochain (2013)).

2.2 Thermodynamic availability

For homogeneous single phase thermodynamical systems, the entropy function \( S(Z) \) (3) is necessarily concave along the equilibrium evolutions (Callen (1985)). This property (independent of chemical reaction and variation rate) is an extension of the second law of thermodynamics. From the concavity of the entropy function \( S(Z) \), it can be shown (Ruszkowski et al. (2005); Hoang et al. (2011)) that the function named the thermodynamic availability \( \mathcal{A} \) defined as follows:

\[
\mathcal{A}(Z, Z^*) = S(Z^*) + w^T(Z - Z^*) - S(Z) \geq 0 \quad (13)
\]

where \( Z^* \) is some fixed reference point (for example the desired set point for control), is non negative. Furthermore, it may be noted that the thermodynamic availability defined on the basis of the entropy function as seen in (13) is thus an extensive variable. The availability concept can be traced back at least to (Keenan (1951); Ydstie (2001)) and more recently in (Hoang et al. (2012)).

In our previous works (Hoang et al. (2011, 2012)), we have shown that the availability \( \mathcal{A} \) defined in (13) can be used as a candidate Lyapunov function to stabilize continuous stirred tank reactors (CSTRs) at the desired state \( Z^* \) for a large range of operating conditions. In this paper, we extend this concept and show how it can be used to control tubular reactors. Taking into account the distributed parameter nature of tubular reactors, the non negative availability density of the global quantity defined in (13) is given by:

\[
a(z, z^*) = s(z^*) + w^T(z - z^*) - s(z) \geq 0 \quad (14)
\]

where \( w^T = w(z^*) \) is defined by using (11) and \( z^* \) is the desired stationary profile for the control design.

Together with (Hp1) and (Hp2), we use an additional hypothesis:

(Hp3) The reaction system is under isochore conditions.

Finally, the bulk thermodynamic availability of distributed parameter systems is defined throughout its density given in (14) as follows:

\[
\mathcal{A} = \int_V \rho a dV \quad (15)
\]

It can be shown from (14) that the bulk thermodynamic availability \( \mathcal{A} \) defined in (15) is non-negative. Consequently, the bulk thermodynamic availability (15) can be used as a storage function candidate for the stabilization of distributed parameter reaction systems at the desired stationary profile \( z^* \) if and only if its time derivative is negative:

\[
\frac{d \mathcal{A}}{dt} < 0 \quad (16)
\]

In what follows, a tubular reactor involving one chemical reaction is considered as an illustrative example to show the application of the developments. The control design is mainly based on the global stabilizing condition (16).

3. CASE STUDY: A TUBULAR REACTOR

3.1 Mathematical model

Let us consider the one dimensional model of a tubular reactor as sketched in Figure 1 in which an irreversible chemical reaction involving two species \( X_1 \) and \( X_2 \) takes place. The reaction stoichiometry is expressed as follows:

\[
\nu_1 X_1 + \nu_2 X_2 = 0 \quad (17)
\]

where \( \nu_k \) is the signed stoichiometric coefficient (Hoang et al. (2011)).

![Fig. 1. A plug flow reactor in the axial direction x](image)

Some additional assumptions are made to derive the mathematical model of the tubular reactor:

(Hp4) The reaction mixture is (locally) ideal.

(Hp5) The total mass density \( \rho \) and the barycentric velocity\(^3 \) \( \nu \) are assumed to be constant.

In this case, the thermodynamic variables (7) are completely given as follows:

\[
z = \left( h, \omega_1, \omega_2 \right)^T \quad \text{and} \quad w = \left( \frac{1}{T}, -\frac{\mu_1}{T}, -\frac{\mu_2}{T} \right)^T \quad (18)
\]

Besides the dynamical behaviour of the reaction system can be derived by using the energy and material balance equations. The dynamical model of the tubular reactor is then given by the following partial differential equations (De Groot and Mazur (1962)):

\[
\frac{\partial \rho z}{\partial t} = -\frac{\partial f}{\partial x} + \sigma \quad (19)
\]

with

\[
f = f_d + f_c, \quad \sigma = (0, \nu_1 r_v, \nu_2 r_v)^T \quad (20)
\]

where \( r_v \) is the reaction rate. \( f_d \) and \( f_c \) are the diffusive and convective fluxes, respectively:

\[
f_d = \left( J_{q_1}, J_{q_1}, J_{q_2} \right)^T, \quad f_c = \nu_b \rho \left( h, \omega_1, \omega_2 \right)^T \quad (21)
\]

\(^3\) It is also referred as fluid velocity.
(20)(21) represent the constitutive equations of the dynamics (19). Note that the following relation holds for all diffusion fluxes within the mixture due to the difference of the proper velocity of the species \( k \) and the fluid velocity (De Groot and Mazur (1962)):
\[
J_i^f + J_i^d = 0 \tag{22}
\]
The system (19) is then completed by the boundary and initial conditions as follows:

Danckwerts’ boundary conditions
\[
\begin{align*}
(v_b \rho h)_{x=0^-} &= \left( J_0 + v_b \rho h \right)_{x=0^+} \\
(v_b \rho \omega_1)_{x=0^-} &= \left( J_1^f + v_b \rho \omega_1 \right)_{x=0^+} \\
(v_b \rho \omega_2)_{x=0^-} &= \left( J_2^f + v_b \rho \omega_2 \right)_{x=0^+} \\
(J_0)_{x=L} &= \left( J_1^d \right)_{x=L} = \left( J_2^d \right)_{x=L} = 0 
\end{align*} \tag{23}
\]
Initial conditions
\[
\begin{align*}
\rho h(x,0) &= \rho h^0(x) \\
\rho \omega_1(x,0) &= \rho \omega_1^0(x) \\
\rho \omega_2(x,0) &= \rho \omega_2^0(x) 
\end{align*} \tag{24}
\]
In the remaining of the paper, we let the notation \( \tilde{\bullet} \) be the deviation form with respect to some desired reference value:
\[
\tilde{\bullet} = (\bullet) - (\bullet)^* \tag{25}
\]

3.2 Dynamics of the availability

The bulk thermodynamic availability defined in (15) associated with the tubular reactor (Figure 1) can be rewritten as follows:
\[
\mathcal{A} = \int_0^L \rho a A_S dx \geq 0 \tag{26}
\]
where \( A_S \) is the (constant) cross section.

Proposition 1 allows us to calculate the time derivative of the bulk thermodynamic availability defined in (26). We shall see that its variation rate depends not only on boundary exchanges but also on the internal transformations due to the transport phenomena and chemical reaction.

Proposition 1. The time variation of the bulk thermodynamic availability (26) of the reaction system defined by (19)-(21) is given by:
\[
\frac{dA}{dt} = \left( \left[ \tilde{w}^T f \right]_\Omega - \left( < \tilde{f}, \tilde{X} >_{\Omega} + < \tilde{\sigma}, \tilde{w} >_{\Omega} \right) \right) A_S 
\]
where \( \Omega = [0 \ 1] \) and the thermodynamic driving force indicated with \( \tilde{X} \) appeared in (27) is defined as follows:
\[
\tilde{X} = \frac{\partial w}{\partial x} \tag{28}
\]
Proof. By using (9), the expression of the availability density (14) can be rewritten in the following form:
\[
a = -s(z) + w^T z \tag{29}
\]
Thanks to the HLE and the (local) Gibbs equation (8), one can apply the material derivative denoted by \( \frac{D}{Dt} = \frac{D}{dt} + \frac{\partial}{\partial t} \) and
\[
v_b \frac{D}{Dt} \tag{De Groot and Mazur (1962))}
\]
for both sides of (29) due to the axial motion resulting from the fluid velocity \( v_b \). By multiplying the resulting equation by the total mass density \( \rho \), one obtains:
\[
\rho \frac{D}{Dt} = -(w - w^*)^T \rho \frac{Dz}{Dt} + \frac{\partial w^*}{\partial x} \frac{D}{Dt} v_b \rho z \tag{30}
\]
From this, by adding the stationary dynamics \( \frac{\partial w^*}{\partial t} \equiv 0 \) into (30), one gets after some simple calculations:
\[
\frac{\partial p_a}{\partial t} + v_b \frac{\partial p_a}{\partial x} = -w^T \frac{\partial \rho z}{\partial t} - w^T v_b \rho z + \frac{\partial w^*}{\partial x} \frac{D}{Dt} v_b \rho z \tag{31}
\]
where \( \rho \frac{D}{Dt} = \frac{\partial p_a}{\partial t} + v_b \frac{\partial p_a}{\partial x} \) has been used.

Note that:
\[
\left\{ \begin{array}{l}
\frac{\partial p_a}{\partial t} = -w^T \frac{\partial \rho z}{\partial t} \\
-w^T v_b \frac{\partial \rho z}{\partial x} + \frac{\partial w^*}{\partial t} v_b \rho z + \frac{\partial w^*}{\partial x} v_b \rho z = 0
\end{array} \right. \tag{32}
\]
since \( a = -w^T z \) (9)(29) and the (local) Gibbs-Duhem equation (10) implies that the equality \( \frac{\partial w^*}{\partial t} v_b \rho z \equiv 0 \) holds (Curtiss and Bird (1999)). Consequently, from (31) we have:
\[
\frac{\partial p_a}{\partial t} = -w^T \frac{\partial \rho z}{\partial t} \tag{33}
\]
By taking the balance equations (19) into account and if we note that \( \frac{\partial w^*}{\partial t} = \frac{\partial w^*}{\partial x} f + w^T \frac{\partial f}{\partial x} \), (33) becomes:
\[
\frac{\partial p_a}{\partial t} = \frac{\partial w^*}{\partial x} f - \left( f^T \tilde{X} + \tilde{\sigma}^T \tilde{w} \right) \tag{34}
\]
which yields the desired result as seen in (27) by integration over the overall volume. \( \square \)

Remark 1. Due to the presence of the cross section \( A_S \), the diffusive flux \( f_d \) and the convective flux \( f_c \), the proposed result (27) completes the formulation presented in (Alonso and Ydstie (2001); Ruszkowski et al. (2005)).

As previously shown, the bulk availability \( \mathcal{A} \) (26) is non-negative. It is worth noting that if the right side of (27) can be shaped to be negative then the tubular reactor is globally stabilized at its desired reference profile \( z^* \).

3.3 Stabilization via boundary control

Let us state the following proposition. Its development is general.

Proposition 2. The reaction system defined by (19)-(21) is (strictly) passive with respect to its input-output pair selected as,
\[
u = \left( \begin{array}{c}
-f(0,t) \\
f(L,t)
\end{array} \right), \quad y = \left( \begin{array}{c}
\tilde{w}(0,t) \\
\tilde{w}(L,t)
\end{array} \right) \tag{35}
\]
and a storage function \( W(t) \) defined as,
\[
W(t) = \frac{\mathcal{A}(t)}{A_S} \tag{36}
\]
if and only if the dissipative term \( \check{d} \) given by
\[
\check{d} = \check{f}, \tilde{X} >_{\Omega} + < \check{\sigma}, \tilde{w} >_{\Omega} \tag{37}
\]
fulfills the following condition,
\[
\check{d} \geq 0 \tag{38}
\]
Consequently, the following proportional feedback control law:
\[ u = -Ky \] (39)
with the gain matrix \( K = K^T > 0 \), stabilizes the reactor at the desired state \( z^* \).

**Proof.** We can easily check that the time variation of the bulk thermodynamic availability presented in (37) reduces to the following simple form by using (35)(36):
\[ \frac{dW(t)}{dt} = u^Ty - \left( < \tilde{f}, \tilde{X} >_{\Omega} + < \tilde{\sigma}, \tilde{w} >_{\Omega} \right) \] (40)
From (37) and the dissipation condition given in (38), (40) is bounded from above as follows:
\[ \frac{dW(t)}{dt} \leq u^Ty \] (41)
Hence the system is (strictly) passive (Van Der Schaft (2000); Brogliato et al. (2007)). From this, the proportional feedback law (39) renders the system dissipative since \( y^T[-K]y < 0 \). The latter completes the proof. \( \Box \)

**Remark 2.** The dissipation condition (38) is indeed strongly related to transport phenomena and kinetic reactions.

For the sake of illustration, let us check the dissipative condition (38) for a simple case without convection since convective fluxes never create the entropy (De Groot and Mazur (1962)). In this case, (38) takes the simple form:
\[ \frac{dW(t)}{dt} = u^Ty - \tilde{d} \] (42)
and the dissipation term \( \tilde{d} \) defined in (37) becomes:
\[ \tilde{d} = < \tilde{f}, \tilde{X} >_{\Omega} + < \tilde{\sigma}, \tilde{w} >_{\Omega} \] (43)
where \( \tilde{f} = \tilde{f}_d \) has been used since \( v_b = 0 \Rightarrow \tilde{f}_c = 0 \). We may note at this point that the sign of the dissipation term (43) depends on the explicit form of constitutive relations of the diffusive vector \( f_d \) and the production rate vector \( \sigma \) defined in (20). Thanks to phenomenological relations directly obtained from the positivity of \( \Sigma \) (12), their explicit forms are expressed with respect to the thermodynamic variables (see (B.1)(B.2) in Appendix B) as follows:
\[ f_d = L_d X, \quad \sigma = K_r w \] (44)
As a consequence, we have:
\[ \tilde{f}_d = L_d \tilde{X}, \quad \tilde{\sigma} = K_r \tilde{w} \] (45)
Note that results in (45) are obtained only if the linear domain is considered for (44). This is particularly the case when the system states are near the desired stationary equilibrium \( z^* \) so that the matrices \( L_d \) and \( K_r \) are constant ones. Furthermore, the matrices \( L_d \) and \( K_r \) meet the following properties (see (A.10)(B.3) in Appendices A and B):
\[ L_d = L_d^T \geq 0, \quad K_r = K_r^T \geq 0 \] (46)
On the basis of the relations given in (45)(46), the dissipation term (43) takes the simple form as follows:
\[ \tilde{d} = \int_0^L \tilde{X}^T L_d \tilde{X} \, dx + \int_0^L \tilde{w}^T K_r \tilde{w} \, dx \geq 0 \] (47)
Consequently, (38) holds.

**4. CONCLUSION**

In this paper, we have shown by means of the passivity based approach how to stabilize distributed parameter reaction systems using the thermodynamic foundations. In particular, the boundary control problem of the tubular reactors can be formulated by assigning the boundary fluxes and the boundary intensive variables as the control input and the controlled output, respectively. The system is then (strictly) passive with respect to a storage function strongly related to the availability if and only if the dissipation condition holds. Hence a simple proportional feedback law renders the system dissipative and consequently, the reactor is globally stabilized at the desired stationary profile. It has been verified, in our first studies without convection, that this dissipation condition is guaranteed thanks to the linear phenomenological relations directly derived from the entropy production. It remains now to extend the proposed developments to the multiple chemical reaction system and the more general case where nonlinear phenomenological relations (in particular, nonlinear reaction kinetics) and convection are present. Our first studies show that such a situation may destroy the dissipation condition (38).

**Appendix A. PHENOMENOLOGICAL EQUATIONS**

From the (local) Gibbs equation (8) and by using (19)-(22), the entropy balance (12) is explicitly described with:
\[ J_{s,tot} = \frac{1}{T} \left( J_q - \sum_{k=1}^2 \mu_k q_k^d + \rho \mu v_b s \right) \] (A.1)
\[ \Sigma_s = -J_d \frac{\partial \frac{u}{q} \mu_s}{\partial x} + J_q \frac{\partial \frac{1}{T} \rho \sigma_s}{\partial x} - \frac{1}{T} \sum_{k=1}^2 r_v \nu_k \mu_k \geq 0 \] (A.2)
Moreover, the affinity of the reaction (17) that represents an extended thermodynamic force is defined as follows:
\[ \sigma_m = (\nu_1 \mu_1 + \nu_2 \mu_2) \] (A.3)
From definition (A.3), (A.2) therefore becomes:
\[ \Sigma_s = -J_d \frac{\partial \frac{u}{q} \mu_s}{\partial x} + J_q \frac{\partial \frac{1}{T} \rho \sigma_s}{\partial x} - r_v \sigma_m \geq 0 \] (A.4)
Let us note that \( \Sigma_s \) (A.2) (or (A.4)) remains valid for any evolution. Taking into account the cross-effects between heat conduction and diffusion and the positivity of the irreversible entropy production (A.4), we obtain for phenomenological equations (De Groot and Mazur (1962)):
\[
\begin{align*}
J_q &= L_{qq} \frac{\partial}{\partial x} - L_{q1} \frac{\partial \frac{u}{q} \rho \sigma_s}{\partial x} \\
J_d &= L_{1d} \frac{\partial}{\partial x} - L_{11} \frac{\partial \frac{u}{q} \mu_s}{\partial x} \\
r_v &= -L_r \sigma_m \frac{\partial}{\partial x}
\end{align*}
\] (A.5)
where \( L_{qq}, L_{q1}, L_{1d}, L_{11} \) and \( L_r \) are the phenomenological coefficients. In general, they depend on the thermodynamic variables (temperature and concentrations etc.).

With the help of (22)(A.3) and by introducing the phenomenological equations (A.5) into (A.2), \( \Sigma_s (A.2) \) is then given by the following quadratic form:
\[ \Sigma_s = X_s^T \left( \frac{L_d}{0} \frac{L_1}{L_r} \right) X_s \geq 0 \] (A.6)

\[ 4 \] This phenomena is described by the Curie principle (De Groot and Mazur (1962)).
where the generalized thermodynamic force vector $X_s$ is defined as follows:

$$X_s = \left( X^T \frac{\partial q_m}{\partial T} \right)^T$$  \hspace{1cm} (A.7)

In (A.6)(A.7), we use:

$$X = \frac{\partial w}{\partial x} = \left( \frac{\partial q_1}{\partial x} \frac{\partial q_2}{\partial x} \frac{\partial q_3}{\partial x} \right)^T$$  \hspace{1cm} (A.8)

and

$$L_d = \begin{pmatrix} L_{q1} & L_{q2} & -L_{q1} \\ L_{1q} & L_{11} & L_{12} \\ -L_{1q} & L_{11} & L_{12} \end{pmatrix}$$  \hspace{1cm} (A.9)

A sufficient condition that guarantees the positivity of the irreversible entropy production shown in (A.6) is:

$$\begin{cases} L_d = L_d^T \geq 0 \\ L_r = L_r^T \geq 0 \end{cases}$$  \hspace{1cm} (A.10)

The requirement (A.10) meets the so-called Onsager reciprocal relations (De Groot and Mazur (1962)).

Appendix B. CONSTITUTIVE RELATIONS

The diffusive flux vector can be written by using (21)(A.5):

$$f_d = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = L_d X$$  \hspace{1cm} (B.1)

where the thermodynamic force $X$ and the matrix $L_d$ are given in (A.8)(A.9), respectively.

Finally thanks to (A.3)(A.5), the production rate vector $\sigma$ (20) is expressed as follows:

$$\sigma = K_r^T w$$  \hspace{1cm} (B.2)

with

$$K_r = \begin{pmatrix} 0 \\ \nu_1 \\ \nu_2 \end{pmatrix} L_r \begin{pmatrix} 0 & \nu_1 & \nu_2 \end{pmatrix}$$  \hspace{1cm} (B.3)

Consequently, $K_r = K_r^T \geq 0$ since $L_r \geq 0$ from (A.10).

REFERENCES


