Irreversible port-Hamiltonian Approach to Modeling and Analyzing of Non-isothermal Chemical Reaction Networks

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Abstract: Inspired by great advances on the mathematical structure of chemical reaction networks governed by mass action kinetics and by one of the main features of Irreversible port-Hamiltonian formulation that the thermodynamic principles could be presented clearly and directly in its structure, the aim of our work is to utilize the Irreversible port-Hamiltonian formulation to study chemical reaction networks in non-isothermal case, including modeling, equilibrium and asymptotic stability.

Keywords: Chemical reaction network, Irreversible port Hamiltonian systems, Equilibrium, Lyapunov function, Asymptotic stability

1. INTRODUCTION

With its great potential in various application domains, chemical reaction networks have been a popular subject in recent years. Progress has been made on the mathematical structure of isothermal chemical reaction networks governed by mass action kinetics, see Van der Schaft et al. (2013), Van der Schaft et al. (2015) and Rao et al. (2013). Nevertheless, there remain some challenges in the study of the chemical reaction networks in non-isothermal case which would grant us a comprehensive understanding of its dynamics. As commonly understood, in non-isothermal case, some thermodynamic principles of chemical reaction networks should be taken into consideration when we investigate its modeling and stability analysis.

Port Hamiltonian systems (PHS), which is a very important tool for the control of nonlinear systems, has been intensively employed in modeling and passivity-based control (PBC) of electrical, mechanical and electromechanical domains (Maschke and Van der Schaft (1991),Van der Schaft and Maschke (1995) and Schaft (2006)). More recently, an energy based quasi-PHS model, namely Irreversible port-Hamiltonian System(IPHS) was proposed (Ramirez et al. (2013)). Thanks to its formulation which is directly related with the energy and entropy functions, IPHS could be easily utilized for thermodynamic, chemical and biological systems. Therefore we are naturally inspired to apply it to non-isothermal chemical reaction networks.

In this paper, we implement certain results of IPHS and its stability analysis to a non-isothermal chemical reaction networks. Beginning with the mathematical structure of chemical reaction networks in the non-isothermal case, we establish its IPH formulation and then investigate some balanced analysis, including the equilibrium and the asymptotic stability.

The paper is organized as follows: Section 2 presents the mathematical structure of non-isothermal chemical reaction networks. The framework of IPHS and its specialization to non-isothermal chemical reaction networks are introduced in Section 3. Section 4 focuses mainly on the balanced analysis, including the set of equilibria and the energy based availability function generated by the internal energy. In Section 5 we demonstrate the effectiveness of our proposed approach by applying it to a simple non-isothermal chemical reaction network. Finally Section 6 provides some closing remarks and lines of future work.

2. CHEMICAL REACTION NETWORK STRUCTURE

In this section, we first survey some definitions about chemical reaction networks mentioned in Ramirez et al. (2013), Couenne et al. (2006) and Van der Schaft et al. (2013) which will be used in the following sections.

Consider a chemical reaction network composed by r reactions, m species and c complexes with the following reversible reaction scheme:

$$\sum_{i=1}^{m} \alpha_{ij} A_i \overset{j}{\rightleftharpoons} \sum_{i=1}^{m} \beta_{ij} A_i, j = 1...r \quad (1)$$

with α_{ij}, β_{ij} being the constant stoichiometric coefficients for species A_i of the jth chemical reaction.

We define a state vector, denoted as $x = [x_1, x_2...x_m]^T \in \mathbb{R}_+^m$ where x_i denotes the concentration of the ith species; an $m \times r$ matrix S, named as the stoichiometric matrix whose (i,j)th element is the signed stoichiometric coefficient of the ith species in the jth reaction; an $m \times c$ matrix Z, named as the complex stoichiometric matrix whose ρth column captures the expression of the ρth complex in the ith chemical species; an $c \times r$ matrix B, called the incidence matrix, whose (i,j)th element equal to -1 if vertex i is the tail vertex of edge j and 1 if vertex i is the head vertex of edge j, while 0 otherwise. Besides, for the jth chemical reaction, let Z_{S_j} and Z_{P_j} denote the columns of the complex stoichiometry matrix Z corresponding to the substrate complex S_j and the product complex P_j. Note that we have $\alpha_{ij} = Z_{iS_j}$ and $\beta_{ij} = Z_{iP_j}$.

The reaction rate of the jth reaction of a chemical reaction network is considered to be a combination of the forward reaction with forward rate equation $v_j^f = k_j^f(T) \prod_{i=1}^{m} x_i^{\alpha_{ij}}$ and the backward reaction with rate equation $v_j^b = k_j^b(T) \prod_{i=1}^{m} x_i^{\beta_{ij}}$. The coefficients $k_j^f(T)$ and $k_j^b(T)$ follow the Arrhenius equation :

$$k_j^f(T) = k_j^f \exp(\frac{-E_j^f}{RT})$$

$$k_j^b(T) = k_j^b \exp(\frac{-E_j^b}{RT})$$

for some constants k_j^f, k_j^b, E_j^f, E_j^b and R, see Couenne et al. (2006).

Let us define the element-wise natural logarithm Ln: $\mathbb{R}_+^m \mapsto \mathbb{R}^m$, $x \mapsto Ln(x)$, as the mapping whose ith element component is given as $(Ln(x))_i := \ln(x_i)$. With this notation, the reaction rate of the jth reaction of a chemical reaction network, from a substrate complex to a product complex, can be written as

$$\begin{aligned} r_j(x,T) &= k_j^f(T) \prod_{i=1}^{m} x_i^{\alpha_{ij}} - k_j^b(T) \prod_{i=1}^{m} x_i^{\beta_{ij}} \\ &= k_j^f(T) \exp(Z_{S_j}^T Ln(x)) - k_j^b(T) \exp(Z_{P_j}^T Ln(x)) \\ &= k_j^f \exp(Z_{S_j}^T Ln(x) - \frac{E_j^f}{RT}) - k_j^b \exp(Z_{P_j}^T Ln(x) - \frac{E_j^b}{RT}) \end{aligned} \quad (2)$$

3. IRREVERSIBLE PORT-HAMILTONIAN FORMULATION FOR NON-ISOTHERMAL CHEMICAL REACTION NETWORKS

In general, IPHS can be defined by the following state equation (Ramirez (2012), Ramirez et al. (2013)):

$$\dot{x} = R(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})J\frac{\partial U}{\partial x}(x) + W(x, \frac{\partial U}{\partial x}) + g(x, \frac{\partial U}{\partial x})u(t) \quad (3)$$

Here $x \in \mathbb{R}^n$ is the state vector, $U(x) : C^\infty(\mathbb{R}^n) \to \mathbb{R}$, $S(x) : C^\infty(\mathbb{R}^n) \to \mathbb{R}$ and $J \in \mathbb{R}^n \times \mathbb{R}^n$ is a constant skew-symmetric matrix. The expression $R = R(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})$ is composed of a positive definite function and a Poisson bracket evaluated on S and U, as follows

$$R(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}) = \gamma(x, \frac{\partial U}{\partial x})\{S, U\}_J \quad (4)$$

with $\gamma(x, \frac{\partial U}{\partial x}) = \hat{\gamma}(x) : C^\infty(\mathbb{R}^n) \to \mathbb{R}$, a nonlinear positive function of the states and co-states of the system. The term $g(x, \frac{\partial U}{\partial x})u(t)$ denotes the port of the system where the input $u(t) \in \mathbb{R}^m$ is a time dependent function.

The IPH formulation above can be rewritten in a specific way for chemical reaction networks (Ramirez et al. (2013)). The dynamical equation of a chemical reaction network (1) defined by the mass and entropy balance equations, can be expressed as

$$\begin{aligned} \dot{x} &= (\sum_{j=1}^{r} R_j(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})J_j)\frac{\partial U}{\partial x}(x) + g(x, \frac{\partial U}{\partial x})u(t) \\ &= J_R(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})\frac{\partial U}{\partial x}(x) + g(x, \frac{\partial U}{\partial x})u(t) \end{aligned} \quad (5)$$

with state vector $x = [x_1 \ldots x_m \ S]^T$ and $\frac{\partial U}{\partial x} = [\mu_1 \ldots \mu_m \ T]^T$, and with the internal energy $U(x)$ as Hamiltonian function. The constant skew-symmetric matrix J_j is given by

$$J_j = \begin{bmatrix} 0 & \cdots & 0 & \bar{\nu}_1 \\ 0 & \cdots & 0 & \vdots \\ 0 & \cdots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \cdots & -\bar{\nu}_m & 0 \end{bmatrix} \quad (6)$$

where $\bar{\nu}_i = S_{ij}, i = 1, ..., m$. Therefore the term J_R can be expressed as

$$J_R = \sum_{j=1}^{r} R_j(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})J_j = \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & S\overrightarrow{R} \\ 0 & \cdots & 0 & \\ -(S\overrightarrow{R})^T & & 0 \end{bmatrix} \quad (7)$$

where S is the stoichiometric matrix and the jth element of the vector $\overrightarrow{R}$ is given by

$$R_j = \gamma_j(x, \frac{\partial U}{\partial x})\{S, U\}_{J_j} = (\frac{r_j}{T\mathcal{A}_j})\mathcal{A}_j \quad (8)$$

with

$$\mathcal{A}_j = -\sum_i S_{ij}\mu_i$$
$$r_j = k_j^f \exp(Z_{S_j}^T Ln(x) - \frac{E_j^f}{RT}) - k_j^b \exp(Z_{P_j}^T Ln(x) - \frac{E_j^b}{RT}) \quad (9)$$

where $\mathcal{A}_j = \{S, U\}_{J_j}$ is the chemical affinity of the jth reaction and corresponds to the thermodynamic driving force of the chemical reaction and the r_j is the reaction rate of the jth chemical reaction based on equation (2). The port of the IPHS for a chemical reaction network can be shown to be given as:

$$g(x, \frac{\partial U}{\partial x}, u) = \begin{bmatrix} \overrightarrow{F_e} - \overrightarrow{F_s} \\ S_{in} - S_{out} \end{bmatrix}$$

where $\overrightarrow{F_e} = (F_{e1}, \cdots, F_{em})^T$ and $\overrightarrow{F_s} = (F_{s1}, \cdots, F_{sm})^T$ denote the $m \times 1$ vector of inlet/outlet molar flows; S_{in} and S_{out} are respectively the entropy carried into the reactor by external sources and out of the reactor to external environments.

Consequently, the IPH formulation for a chemical reaction network can be summairized as