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Irreversible port-Hamiltonian formulation of chemical reaction networks

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***Abstract*— Reaction networks refers to multiple reactions, like chemical, biochemical, biological etc., occurring simultaneously in a reactor. Traditional studies consider mainly isothermal operation conditions, thus focussing on the dynamics of the interconnected mass balance laws. This is however an unrealistic scenario in most real life applications since thermal gradients are often one of the main driving forces of any kind of reaction. In a recent work the set of dynamic equations governing the evolution of a general single chemical reaction has been modelled as irreversible port-Hamiltonian control systems. These systems express, just like standard port-Hamiltonian systems, the conservation of energy as a structural property but in addition they also express (as a structural property) the second law of Thermodynamics: the irreversible production of entropy. In this work the irreversible port-Hamiltonian formulation is extended to general reaction networks, allowing to propose an energy based model for non-isothermal reaction networks. The developments are performed for chemical reaction networks, but the model is general and can be applied to any kind of non-isothermal reaction. The results are illustrated on a simple 2 step chemical reaction network.**

I. INTRODUCTION

Reaction networks have been the subject of numerous studies in the last decades. Indeed, the formulation of a general reaction network theory is of great interest for different scientific and industrial domains, such as chemistry, biochemistry and biology. Most of the studies carried out on reaction networks consider that the system is approaching a thermodynamic equilibrium. However, this is a restrictive assumption as Qiana and Beards [1] have pointed out, *"Yet, a majority of thermodynamic analyses and/or kinetic studies focus only on "non-living" systems. By a non-living system, we mean that if one waits a sufficiently long time compared with its relaxation time, the system approaches a thermo-chemical equilibrium. In contrast, a living system cannot be isolated; it is open to energy and material exchange with its surrounding, accompanied with heat dissipation. After a time sufficiently long compared with its relaxation time, an open system approaches to a non-equilibrium steady-state"*. An irreversible thermodynamic approach to model and analyse reaction networks is hence necessary for a deeper understanding of their non-equilibrium dynamics. The works of [2]–[4] were pioneers in introducing network thermodynamics for the analysis of reaction networks. The conservation of energy and irreversible creation of entropy have been used to study biochemical reaction networks from a dynamic system perspective [1] and to constraint optimization based algorithms to reach optimal and also physically admissible operation conditions [5]. Another line of research aims to study the dynamic behaviour of open (controlled) reaction networks by characterizing the network by linear graphs and/or its underlying geometric structure [6]–[8]. In this direction the works of [9]–[11] express isothermal reaction networks as locally dissipative systems with respect to virtual energy and entropy functions. Also along this line, in [12] port-Hamiltonian systems (PHS) [13] are used to propose a control system representation for open reaction networks and in [14] the geometric structure of the network is explored relating it with graph theory and some virtual energy and entropy function to study stability and model reduction.

In this paper a recently proposed energy based model, called Irreversible port-Hamiltonian System (IPHS) [15], [16] is used to model reaction networks. IPHS defines a class of quasi-PHS which encompasses thermodynamic control systems and it is shown, starting from a simple reaction, that a reaction network can be systematically written in IPHS format. One of the main features of IPHS is that they express the first and second principle of thermodynamics, hence the structure of these systems is directly related with the energy and entropy functions. This allows to use to passivity based techniques similarly as for mechanical systems to study dynamic properties such as stability. The paper is organized as follows. Section II presents the basics on chemical reaction networks. In Section III we introduce IPHS. The main result, which is the IPHS of a general reaction network, is given in Section IV. Section V presents and illustrating example and finally some concluding remarks are given in Section VI.

II. CHEMICAL REACTION NETWORKS

Let us first consider a single reaction in a continuous stirred tank reactor with the following reversible reaction scheme

$$\sum_{i=1}^{m} \alpha_i A_i \overset{r}{\rightleftharpoons} \sum_{i=1}^{m} \beta_i A_i$$

with α_i, β_i being the constant stoichiometric coefficients for species A_i in the reaction. The time variation of the species

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in the reactor is given by [17]

$$\dot{n}_i = F_{ei} - F_{si} + r_i V \qquad i = 1, \ldots, m \tag{1}$$

where n_i is the number of moles of the species i, (and $\mathbf{n}$ the vector $\mathbf{n} = (n_1, \ldots, n_m)^\top$). All reactions are assumed to be reversible, with reaction rates obeying the mass action law [6], [7] $r_i = \bar{\nu}_i r$ where $r(\mathbf{n}, T)$ is the reaction rate which is the difference of the forward reaction rate r_f and the backward reaction rate r_b: $r = (r_f - r_b)$ and depends on the temperature and on the reactant mole number, $\bar{\nu}_i$ is the signed stoichiometric coefficient: $\bar{\nu}_i = \alpha_i - \beta_i$, and is positive or negative depending on whether the species i is a product or a reactant in the reaction. F_{ei} and F_{si} are respectively the inlet and outlet molar flows (and $\mathbf{F}_e$ the vector $\mathbf{F}_e = (F_{e1}, \ldots, F_{em})^\top$). Following the usual assumptions [17], [18], V the volume in the reactor is assumed to be constant as well as the pressure. The dynamic evolution of the mole balance can then be represented by a set of ordinary differential equations which in compact matrix form is written as

$$\dot{\mathbf{n}} = CrV + \mathbf{F}_e - \mathbf{F}_i \tag{2}$$

where C is a $m \times 1$ vector called the stoichiometric vector, and whose elements are the signed stoichiometric coefficients of the reaction.

The classical construction of the complete state space of the ideal mixture in the CSTR, i.e., considering the energy balance as well, is based on Gibbs' fundamental relation. Assuming constant volume and pressure of the mixture in the reactor, Gibbs' relation reduces to

$$dU = \sum_{i=1}^{m} \frac{\partial U}{\partial n_i} dn_i + \frac{\partial U}{\partial S} dS \tag{3}$$

where U denotes the internal energy, S the entropy and the conjugated intensive variables are the chemical potential $\frac{\partial U}{\partial n_i} = \mu_i$ and the temperature $\frac{\partial U}{\partial S} = T$. If we consider for instance a chemical reaction and under the assumption of constant volume, the internal energy is

$$U = \sum_{i=1}^{m} n_i [c_{pi}(T - T_0) + u_{0i}], \tag{4}$$

where c_{pi}, u_{0i}, T_0 are respectively the heat capacity at constant pressure, reference molar energy and reference temperature. At constant volume and pressure the reference molar enthalpy is $h_{0i} = u_{0i}$ [19], and the balance equation of the internal energy is [18], [20]

$$\dot{U} = \dot{H} = \sum_{i=1}^{m} (F_{ei} h_{ei} - F_{si} h_{si}) + Q, \tag{5}$$

where $Q = \lambda(T_e - T)$ is the heat flux from the jacket with λ the heat conduction coefficient, T_e the temperature of the jacket, H the total enthalpy of the reactor and h_{ei}, h_{si} respectively the inlet and outlet specific molar enthalpies, which are related with the chemical potentials and the specific molar entropies s_i by:

$$\mu_i = h_i - T s_i.$$

The entropy function on other hand is given by

$$S = \mathcal{C}_p \ln\left(\tfrac{T}{T_0}\right) - R_g \sum_{i=1}^{m} [n_i \ln\left(\tfrac{n_i}{N}\right)] + \sum_{i=1}^{m} (n_i s_{0i}),$$

where $\mathcal{C}_p = \sum_{i=1}^{m} n_i c_{pi}$, T_0, N, s_{0i} and R_g are respectively total heat capacity at constant pressure, reference temperature, total number of moles, reference molar entropy and the ideal gas constant. Hence, the entropy balance equation is given by

$$\dot{S} = \sum_{i=1}^{m} (F_{ei} s_{ei} - F_s s_i) + \frac{Q}{T_e} + \sigma, \tag{6}$$

where s_{ei} and s_i are respectively the inlet molar entropy and the molar entropy of species i, and σ is the irreversible entropy creation due to mass transfer, heat transfer and chemical reactions:

$$\sigma = \sum_{i=1}^{m} \frac{F_{ei}}{T}(h_{ei} - T s_{ei} - \mu_i) + \frac{Q}{T} - \frac{Q}{T_e} - \sum_{i=1}^{m} \mu_i \nu_i \frac{r}{T}.$$

We have taken the example of a chemical reaction, but it should be noticed that since the state space is constructed from Gibb's fundamental relation, the energy and entropy balance equations always fulfil the first and second principle of thermodynamics; i.e. that the total energy is conserved and that the internal entropy creation is always greater or equal to zero. Hence in general it is always possible to write (5) and (6) as

$$\begin{aligned} \dot{U} &= U_{in} - U_{out}, \\ \dot{S} &= S_{in} - S_{out} + \sigma \end{aligned} \tag{7}$$

where U_{in}, S_{in}, U_{out}, S_{out} are respectively the energy and entropy carried in to the reactor by external sources and out of the reactor to external sinks. The entropy creation on other hand is due to the internal irreversible processes and is completely characterised by the nature and geometry of the specific process.

Let us now consider a chemical reaction network [11] involving m chemical species, among which m_r chemical reactions take place

$$\sum_{i=1}^{m} \alpha_{ij} A_i \overset{r_j}{\rightleftharpoons} \sum_{i=1}^{m} \beta_{ij} A_i, \quad j = 1, \ldots, m_r. \tag{8}$$

with α_{ij} and β_{ij} being the constant stoichiometric coefficients for species A_i in the reaction step j. The linear combinations of the species in (8), namely $\sum_{i=1}^{m} \alpha_{ij} A_i$ and $\sum_{i=1}^{m} \beta_{ij} A_i$, for $j = 1, \ldots, m_r$ are called the complexes. Many fundamental studies on the dynamic behaviour of reaction networks has been carried out by defining the complexes to be the vertices of a directed graph [6]–[8], [11], [14]. The basic structure underlying the dynamics of the vector $\mathbf{n}$ of mole numbers of the chemical species is given by the mass balance law:

$$\dot{\mathbf{n}} = \mathbf{C} \mathbf{r} V + \mathbf{F}_e - \mathbf{F}_s, \tag{9}$$

where the $m \times m_r$ matrix $\mathbf{C}$ is called the stoichiometric matrix whose columns are the stoichiometric vectors of each reaction: $\mathbf{C} = [C_1, C_2, \ldots, C_{mr}]$, and $\mathbf{r} = [r_1, r_2, \ldots, r_{m_r}]^\top$ is the vector whose elements are the reaction rates of each individual reaction. The energy and entropy balance will be given by (7), with each input and output term given by the sum of the input sources and output sinks and where the total internal entropy production will be given by the sum of the internal entropy production of each reaction.

III. IRREVERSIBLE PORT-HAMILTONIAN SYSTEMS

On the state space $\mathbb{R}^n \ni x$, a PHS is defined in the case of power preserving systems by the following state equation,

$$\dot{x} = J(x)\frac{\partial U}{\partial x}(x) + g(x)u(t) \tag{10}$$

where $U : \mathbb{R}^n \to \mathbb{R}$ is the Hamiltonian function that is usually the total energy of the system, $J(x) \in \mathbb{R}^n \times \mathbb{R}^n$ is a skew-symmetric structure matrix, $g(x) \in \mathbb{R}^m \times \mathbb{R}^n$ is the input vector field and $u(t) \in \mathbb{R}^m$ is a time dependent input. For those systems, the Hamiltonian function represents the total energy of the system and the skew-symmetric structure matrix represents the energy flows between the different energy domains of the system. Furthermore the structure matrix $J(x)$ relates to symplectic geometry as it defines a Poisson bracket, if it satisfies the Jacobi identities, else it is a pseudo-Poisson bracket (see [21]). If J is constant in some local coordinates then it satisfies the Jacobi identities [22]. In the sequel we will consider only true Poisson brackets (not pseudo-Poisson brackets). The Poisson bracket of two $C^\infty(\mathbb{R}^n)$ functions Z and G is expressed as:

$$\{Z, G\}_J = \frac{\partial Z}{\partial x}^\top(x) J(x) \frac{\partial G}{\partial x}(x). \tag{11}$$

The PHS dynamics is expressed in term of the Poisson bracket (11) as:

$$\dot{x} = \{x, U\}_J + g(x)u(t). \tag{12}$$

The properties of Poisson brackets such as their skew-symmetry and the fact they satisfy Jacobi identities correspond to the existence of conservation laws or balance equations for open systems. For instance the conservation of the energy is the base of the control using PBC methods [23]. Several attempts have been made in order to preserve as much as possible the PH structure when dealing with thermodynamic systems, leading to a class of systems called *quasi-PHS* [9], [10], [24]–[26]. These systems retain as much as possible the port Hamiltonian structure, but differ by their structure matrices and input vector fields which depend explicitly on the gradient of the Hamiltonian. An important remark is that, although the forms of PHS (10) and quasi-PHS are very similar and both embed, by skew-symmetry of the structure matrix, the conservation of energy, in the latter the drift dynamic is a *nonlinear function* in the gradient $\frac{\partial U}{\partial x}(x)$. In this sense the symplectic structure of the PHS, given by the Poisson tensor associated with the structure matrix $J(x)$, is destroyed.

There is a large class of thermodynamic systems that can be expressed as quasi-PHS if the Hamiltonian function is selected as a thermodynamic potential such as the internal energy or the entropy [15], [27], [28]. From a control perspective it is usually more complicated to impose a desired closed-loop dynamic on quasi-PHS. Passivity based techniques can be easily applied to PHS, however due to the non-linearity with respect to the gradient of the Hamiltonian, this is not the case for quasi-PHS.

In recent works [15], [16] a class of quasi-PHS, denoted Irrevesible Port Hamiltonian Systems (IPHS) have been proposed to model a large class of thermodynamic systems and to embed the first and second principle of Thermodynamics in the structure of the quasi-PHS.

Definition 1: [15], [16] IPHS are defined by the dynamical equation

$$\dot{x} = R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + g\left(x, \tfrac{\partial U}{\partial x}, u\right), \tag{13}$$

where

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

$$R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) = \gamma\left(x, \tfrac{\partial U}{\partial x}\right) \{S, U\}_J, \tag{14}$$

with $\gamma(x, \frac{\partial U}{\partial x}) = \hat{\gamma}(x) : \mathcal{C}^\infty(\mathbb{R}^n) \to \mathbb{R}$, $\hat{\gamma} \geq 0$, a nonlinear positive function of the states and co-states of the system that can be expressed as a function of the states only.
4) $g(x, \frac{\partial U}{\partial x}, u) \in \mathbb{R}^1 \times \mathbb{R}^n$ is associated with the port of the system, where the input is $u(t) \in \mathbb{R}^m$ a time dependent function.

The main difference with the definition of a PHS is that $R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right)$ depends on the co-state variables destroying the linearity of any Poisson tensor, considering the mapping $\frac{\partial U}{\partial x}$ to the drift dynamics $R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}$ and associated with the matrix RJ. Furthermore, the vector field $g\left(x, \frac{\partial U}{\partial x}, u\right)$ may also depend on states and co-states. The first and second principle express, respectively, the conservation of energy and the irreversible transformation of entropy. It is possible to represent this by the following equations

$$\frac{dU}{dt} = 0 \qquad \text{and} \qquad \frac{d\mathfrak{S}}{dt} = \sigma\left(x, \tfrac{\partial U}{\partial x}\right) \geq 0 \tag{15}$$

where the Hamiltonian U is the internal energy, $\mathfrak{S}$ denotes an entropy like function (that may be equal to the total entropy S) and $\sigma\left(x, \frac{\partial U}{\partial x}\right)$ the irreversible entropy creation which in general depends on the state and the differential of the total energy. For IPHS, by skew-symmetry of J the total energy of the system satisfies the energy balance equation

$$\frac{dU}{dt} = \frac{\partial U}{\partial x}^\top g(u(t)).$$

Indeed, since $g(u(t))$ represent the flows through the controlled-ports of the system the only energy variation is due to the interaction with the environment. The entropy variation on the other hand is given by

$$\frac{dS}{dt} = \frac{\partial S}{\partial x}^\top R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) J(x)\frac{\partial U}{\partial x} + \frac{\partial S}{\partial x}^\top g(u(t)).$$

A consequence of the second principle of Thermodynamics is that the entropy variation due to internal transformations is always greater or equal to zero. This actually requires RJ to explicitly depend on $\frac{\partial U}{\partial x}$. Indeed, from Definition 1 we have $R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) = \gamma\left(x, \frac{\partial U}{\partial x}\right)\{S, U\}_J$, hence the internal entropy production, denoted by σ_{int}, is given by

$$\frac{\partial S}{\partial x}^\top RJ\frac{\partial U}{\partial x} = \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\{S, U\}_J^2 = \sigma_{int}, \qquad (16)$$

which is greater or equal to zero for any functions $U(x)$ and $S(x)$ since by definition $\gamma \geq 0$.

IV. IRREVERSIBLE PORT-HAMILTONIAN FORMULATION OF REACTION NETWORKS

Let us start by recalling the IPHS of a simple chemical reaction as proposed in [15]. The dynamical equation of a chemical reaction in a CSTR defined by the mass and entropy balance equations, respectively (2) and (6), can be expressed as the IPHS

$$\dot{x} = RJ\frac{\partial U}{\partial x}(x) + g(x, \tfrac{\partial U}{\partial x}, u) \qquad (17)$$

with state vector $x = [n_1, \ldots, n_m, S]^\top$, the internal energy $U(x)$ as Hamiltonian function, J a constant skew-symmetric matrix whose elements are the stoichiometric coefficients of the chemical reaction mapping the network structure of the reaction,

$$J = \begin{bmatrix} 0 & \ldots & 0 & \bar{\nu}_1 \\ 0 & \ldots & 0 & \vdots \\ 0 & \ldots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \ldots & -\bar{\nu}_m & 0 \end{bmatrix} \qquad (18)$$

and

$$R = \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\{S, U\}_J = \left(\frac{rV}{T\mathcal{A}}\right)\mathcal{A} \qquad (19)$$

with $\gamma = \frac{rV}{T\mathcal{A}}$ and $\{S, U\}_J = \mathcal{A}$, where $\mathcal{A} = -\sum_{i=1}^{m}\bar{\nu}_i\mu_i$ is the chemical affinity of the reaction and corresponds to the thermodynamic driving force of the chemical reaction. The port of the IPHS is given by inlet and outlet of mass and may be modelled simply as $g(x, u)$. Notice that we have not explicitly defined the input u, but it will indeed be related to some input or output flow of mass or/and energy [17]. It is not hard to verify that this dynamical model indeed is an IPHS and that it expresses the mass and entropy (energy) balance laws. We leave the exercise to the reader.

Let us now consider a chemical reaction network. The mass and energy balances are given by (see eq. (9) and (7)):

$$\dot{\mathbf{n}} = \mathbf{C}\mathbf{r}V + \mathbf{F}_e - \mathbf{F}_s,$$
$$\dot{S} = \sigma + S_{in} - S_{out},$$

Let us define a vector containing the the non-linear R_j functions of each reaction:

$$\mathbf{R} \in \mathbb{R}^{m_r} = [R_1, \ldots, R_{m_r}]^\top, \qquad (20)$$

The chemical reaction network can then be formulated as a IPHS from the stoichiometric matrix $\mathbf{C}$ and the vector $\mathbf{R}$ as follows

$$\dot{x} = \underbrace{\begin{bmatrix} 0_m & \mathbf{C}\mathbf{R} \\ -\mathbf{R}^\top\mathbf{C}^\top & 0 \end{bmatrix}}_{J_R}\frac{\partial U}{\partial x} + g(x, u) \qquad (21)$$

with $x = [n_1, \ldots, n_m, S]$ the state vector, $U(x)$ and $S(x)$ respectively the internal energy and the total entropy of the complete reaction network, $g(x, u)$ the vector containing the inputs of the system

$$g(x, u) = \begin{bmatrix} \mathbf{F}_e - \mathbf{F}_s \\ S_{in} - S_{out} \end{bmatrix}, \qquad (22)$$

and 0_m the zero matrix of dimension $m \times m$.

Remark 2: The system (20)-(22) defines a larger class of IPHS than the one contained in Definition 1. Indeed, it is straightforward to verify that for $m_r = 1$ (13) is a particular case of (21).

It is interesting to notice how the structure matrix J_R expresses the energy flow from the material domain to the energy (entropy) domain in a somehow similar manner as a symplectic structure does for mechanical systems [21], [22]. Since $J_R = -J_R$ it's straightforward to verify that the total energy is conserved. The entropy balance on other hand is expected to be (in the case of a closed-reactor) the sum of the entropy productions of each reaction in the network. Indeed, from (21) we have

$$\dot{S} = \frac{\partial S}{\partial x}\dot{x} = \frac{\partial S}{\partial x}J_R\frac{\partial U}{\partial x} = -\mathbf{R}^\top C^\top\mu = \sum_{i=1}^{m_r}\sigma_i \qquad (23)$$

where σ_i is the entropy production due to the i-th chemical reaction. It is also interesting to comment on the fact that unlike traditional representations of reaction networks, which are of dissipative nature [10], [11], [14], the IPHS defines a *conservative* system. This "contradiction" follows since for IPHS the energy (entropy) domain is been considered as part of the state space, and thus the dissipation in the material domain is transformed into entropy creation in the energy domain.

On other hand, and following the same idea as in [16] for coupled mechanical-thermodynamical systems, it is also expected that the dynamical system (21) can be obtained by considering the addition of each individual reaction defined with respect to the complete state space. Indeed, since the temperature in the reactor is common to all reactions, every individual (closed) reaction can be represented by the vector field

$$X_j = R_j J_j(x)\frac{\partial U}{\partial x}(x),$$

with x the state vector of the complete network, $J_j(x)$ the structure matrix and R_j the non-linear function containing the reaction rate of the j-th reaction. The dynamic of the complete reaction is then given by the sum of the vector fields of all individual reactions and the contribution of the input vector field:

$$\dot{x} = \sum_{i=1}^{m_k} X_j + g(x,u) = \underbrace{\left(\sum_{i=1}^{m_r} R_i J_i\right)}_{J_R} \frac{\partial U}{\partial x} + g(x,u).$$

To verify that $\sum_{i=1}^{m_r} R_i J_i = J_R$ it suffices to notice that the term RJ can equivalently be written as

$$RJ = \begin{bmatrix} 0_m & CR \\ -RC^\top & 0 \end{bmatrix},$$

with C the $m \times 1$ stoichiometric vector defined in (2).

V. EXAMPLE: A SIMPLE REACTION NETWORK

Consider the following simple closed reaction network occurring in a CSTR at constant volume

$$\begin{aligned} &\alpha_{11}A_1 + \alpha_{21}A_2 \overset{r_1}{\rightleftharpoons} \beta_{31}A_3, \\ &\alpha_{32}A_3 + \alpha_{42}A_4 \overset{r_2}{\rightleftharpoons} \beta_{52}A_5. \end{aligned} \tag{24}$$

The network reaction scheme may be formulated as an IPHS either by: formulating each individual reaction as an IPH vector field with respect to the complete state space and then "adding" them; or by identifying the stoichiometric matrix of the reaction network and the vector R defined in (20) and immediately obtain J_R. Let us first study the individual reactions. The dynamic of the first reaction is generated by the following vector field

$$X_1 = R_1 J_1 \frac{\partial U}{\partial x}(x) \tag{25}$$

where the state vector is given by the state vector of the *complete* reaction network $x = [n_1, n_2, n_3, n_4, n_5, S]^\top$ and the Hamiltonian is given by the internal energy of the complete system $U(x)$. The structure matrix is given by

$$J_1 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{11} \\ 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{21} \\ 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{31} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\bar{\nu}_{11} & -\bar{\nu}_{21} & -\bar{\nu}_{31} & 0 & 0 & 0 \end{bmatrix}$$

with $\bar{\nu}_{ij} = \alpha_{ij} - \beta ij$, and

$$R_1 = \gamma_1\left(x, \tfrac{\partial U}{\partial x}\right)\{S, U\}_{J_1} = \left(\frac{r_1 V}{T\mathcal{A}_1}\right)\mathcal{A}_1$$

with $\gamma_1 = \frac{r_1 V}{T\mathcal{A}_1}$ and $\{S, U\}_{J_1} = \mathcal{A}_1$, where $\mathcal{A}_1 = -\sum_{i=1,2,3} \bar{\nu}_{i1}\mu_i$ is the chemical affinity (chemical driving force) for the *single* reaction. The dynamic of the second reaction is obtained similarly,

$$X_2 = R_2 J_2 \frac{\partial U}{\partial x}(x) \tag{26}$$

with respect to the following structure matrix

$$J_2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{32} \\ 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{42} \\ 0 & 0 & 0 & 0 & 0 & \bar{\nu}_{52} \\ 0 & 0 & -\bar{\nu}_{32} & -\bar{\nu}_{42} & -\bar{\nu}_{52} & 0 \end{bmatrix}$$

with

$$R_2 = \gamma_2\left(x, \tfrac{\partial U}{\partial x}\right)\{S, U\}_{J_2} = \left(\frac{r_2 V}{T\mathcal{A}_2}\right)\mathcal{A}_2$$

where $\gamma_2 = \frac{r_2 V}{T\mathcal{A}_2}$ and $\{S, U\}_{J_2} = \mathcal{A}_2$, and $\mathcal{A}_2 = -\sum_{i=3,4,5} \bar{\nu}_{i2}\mu_i$. The IPHS of the complete chemical reaction network is given by the sum of the vector fields of each reaction, (25) and (26), and the contribution of the input and outputs flows and the interaction with the cooling jacket, which is all modelled by an input vector field $g(x,u)$:

$$\begin{aligned} \dot{x} &= X_1 + X_2 + g(x,u) \\ &= R_1(x) J_1 \frac{\partial U}{\partial x}(x) + R_2(x) J_2 \frac{\partial U}{\partial x}(x) + +g(x,u) \\ &= \Big(R_1(x) J_1 + R_2(x) J_2\Big) \frac{\partial U}{\partial x}(x) + g(x,u) \\ &= J_R(x) \frac{\partial U}{\partial x}(x) + g(x,u). \end{aligned}$$

with

$$J_R(x) = R_1(x)J_1 + R_2(x)J_2 =$$
$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & R_1\bar{\nu}_{11} \\ 0 & 0 & 0 & 0 & 0 & R_1\bar{\nu}_{21} \\ 0 & 0 & 0 & 0 & 0 & * \\ 0 & 0 & 0 & 0 & 0 & R_2\bar{\nu}_{42} \\ 0 & 0 & 0 & 0 & 0 & R_2\bar{\nu}_{52} \\ -R_1\bar{\nu}_{11} & -R_1\bar{\nu}_{21} & -* & -R_2\bar{\nu}_{42} & -R_2\bar{\nu}_{52} & 0 \end{bmatrix}$$

with $* = R_1\bar{\nu}_{31} + R_2\bar{\nu}_{32}$. The differential of the Hamiltonian is $\frac{\partial U}{\partial x} = [\mu_1, \mu_2, \mu_3, \mu_4, \mu_5, T]$, hence the dynamic of the reaction network is given by

$$\begin{aligned} \dot{n}_1 &= \bar{\nu}_{11} r_1 + F_{e1} - F_{s1}, \\ \dot{n}_2 &= \bar{\nu}_{21} r_1 + F_{e2} - F_{s2}, \\ \dot{n}_3 &= \bar{\nu}_{31} r_1 + \bar{\nu}_{32} r_2 + F_{e3} - F_{s3}, \\ \dot{n}_4 &= \bar{\nu}_{42} r_2 + F_{e4} - F_{s4}, \\ \dot{n}_5 &= \bar{\nu}_{52} r_2 + F_{e5} - F_{s5}, \\ \dot{S} &= -\tfrac{V}{T}\sum_{i=1,2,3} \bar{\nu}_{i1}\mu_i - \tfrac{V}{T}\sum_{i=3,4,5} \bar{\nu}_{i2}\mu_i + S_{in} - S_{out}. \end{aligned}$$

where

$$\sigma_1 = -\tfrac{V}{T}\sum_{i=1,2,3} \bar{\nu}_{i1}\mu_i, \qquad \text{and}$$
$$\sigma_2 = -\tfrac{V}{T}\sum_{i=3,4,5} \bar{\nu}_{i2}\mu_i,$$

correspond to the irreversible entropy production of each individual reaction and which satisfy

$$\sigma_1 + \sigma_2 = \sigma_{tot} \geq 0,$$

with σ_{tot} the total entropy production. Let us now derive the IPH model directly from the stoichiometric matrix $\mathbf{C}$. For the reaction network (24) we have

$$\mathbf{C} = \begin{bmatrix} \bar{\nu}_{11} & 0 \\ \bar{\nu}_{21} & 0 \\ \bar{\nu}_{31} & \bar{\nu}_{32} \\ 0 & \bar{\nu}_{42} \\ 0 & \bar{\nu}_{52} \end{bmatrix}, \qquad \mathbf{R} = \begin{bmatrix} \left(\frac{r_1 V}{T\mathcal{A}_1}\right)\mathcal{A}_1 \\ \left(\frac{r_2 V}{T\mathcal{A}_2}\right)\mathcal{A}_2 \end{bmatrix}$$

From which we directly obtain J_R by using (21).

VI. CONCLUSION

Non-isothermal reaction networks, i.e., in which the irreversible thermodynamic phenomena are not neglected, have been represented as dynamic control systems using the irreversible port-Hamiltonian system (IPHS) representation. The importance of taking into account the irreversible behaviour of a reaction network, which is characterized by the energy balance of the network, relies not only in obtaining better and more realistic models but also in obtaining physically coherent models. Indeed, the change of energy and the evolution of any real system (chemical, biochemical, biological, etc) obey the second law of Thermodynamics and hence the possible trajectories are conditioned by the irreversible processes. Not taking into the energy balance and the dissipative phenomena can lead to for instance physically inadmissible operation points, as reported in [5]. The IPHS model has been derived systematically from the stoichiometry and the reaction rates of the reaction network. The irreversible control system has been developed using as base chemical reaction networks, but the formalism is general and applies to any kind of reaction network. One important implication of this formulation, which "codes" the irreversible nature of the reactions in the structure of the control system, is that standard passivity based techniques may be applied to study the dynamic properties, such as stability or stabilization, of the reaction networks.

Future work will use the IPHS formulation of chemical reaction networks to perform stability analysis and stabilization.

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