

Irreversible Port-Hamiltonian Formulation of some Non-isothermal Electrochemical Processes

3rd IFAC Workshop on Thermodynamic Foundation of Mathematical Systems Theory,
TFMST 2019, Louvain-la-Neuve

Hector Ramirez, Daniel Sbarbaro and Yann Le Gorrec

-
Departamento de Ingeniería Electronica,
Universidad Federico Santa María,
Valparaíso, Chile

July 3, 2019

Energy based modeling and control

Motivations for adopting an **energy-based perspective** in modeling and control

- Physical system can be viewed as a set of **simpler subsystems** that exchange energy through ports,
- Energy is a concept common to all physical domains and is not restricted to linear or non-linear systems: **non-linear** approach,
- Energy can serve as a *lingua franca* to facilitate communication among scientists and engineers from different fields,
- Role of energy and the interconnections between subsystems provide the basis for various control techniques: **Lyapunov based control**.

Conservative systems

[Maschke and van der Schaft, 1992, van der Schaft, 2000]

Port-Hamiltonian control systems

$$\dot{x} = J(x) \frac{\partial U}{\partial x}(x) + gu(t),$$

$$y = g(x)^\top \frac{\partial U}{\partial x}(x)$$

$J(x) = -J(x)^\top$ the interconnection matrix

Balance equations expressed by PHS: Conservation of the **Hamiltonian** and of **Casimir's** of the Poisson bracket

$$\frac{dU}{dt} = \frac{\partial U}{\partial x}^\top gu = u^\top y,$$

$$\frac{dC}{dt} = \frac{\partial C}{\partial x}^\top gu = u^\top y_C$$

Poisson bracket: $\{Z, G\}_J = \frac{\partial Z}{\partial x}^\top(x) J(x) \frac{\partial G}{\partial x}(x)$

Thermodynamic systems

First and **second principle** of thermodynamics

Consider a closed system,

$$\frac{dU}{dt} = 0 \quad \text{and} \quad \frac{dS}{dt} = \sigma \left(x, \frac{\partial U}{\partial x} \right) \geq 0$$

$$\text{for PHS} \quad \frac{dS}{dt} = \frac{\partial S}{\partial x}^\top J \left(x, \frac{\partial U}{\partial x} \right) \frac{\partial U}{\partial x} = \sigma \geq 0, \quad \underline{\text{for any } U(x)}$$

This is the reason to consider **quasi Hamiltonian system**: retain much of the PHS structure, but their structure matrices depend explicitly on the gradient of the Hamiltonian (GENERIC, quasi Hamiltonian systems, Brayton-Mooser formulation,..)

[Germela and Öttinger, 1997, Hangos et al., 2001, Otero-Muras et al., 2008, Eberard et al., 2007, Hoang et al., 2011, Favache and Dochain, 2010]

Irreversible port Hamiltonian systems

A non-linear extension of port Hamiltonian systems

- Ramirez, Maschke and Sbarbaro, Irreversible port-Hamiltonian systems: A general formulation of irreversible processes with application to the CSTR, *Chemical Engineering Science*, 2013. → **Modeling**
- Ramirez, Maschke and Sbarbaro, Modelling and control of multi-energy systems: an irreversible port-Hamiltonian approach. *European Journal of Control* 19 (2013), pp. 513-520. → **Interconnection**
- Ramirez, Le Gorrec, Maschke and Couenne. On the passivity based control of irreversible processes: a port-Hamiltonian approach. *Automatica*, 2016. → **Control**

Irreversible port Hamiltonian systems

IPHS for closed system

$$\dot{x} = R \left(x, \frac{\partial U}{\partial x} \right) J \frac{\partial U}{\partial x} (x)$$

- i. $x \in \mathbb{R}^n$, and $U(x)$ and $S(x)$ relates to the energy and entropy respectively.
- ii. The constant structure matrix $J = -J^T \in \mathbb{R}^n \times \mathbb{R}^n$.

The definition of R

$$R \left(x, \frac{\partial U}{\partial x} \right) = \gamma \left(x, \frac{\partial U}{\partial x} \right) \{S, U\}_J, \quad \gamma \geq 0$$

- $\{S, U\}_J$ defines the thermodynamic driving force
- Entropy balance:

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial x}^T R J \frac{\partial U}{\partial x} = R \{S, U\}_J = \boxed{\gamma \left(x, \frac{\partial U}{\partial x} \right) \{S, U\}_J^2 = \sigma \geq 0}.$$

Irreversible port Hamiltonian systems (Ramirez et al., 2012)

IPHS for open systems

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

- i. $x \in \mathbb{R}^n$, and $U(x), S(x) : \mathbb{R}^n \rightarrow \mathbb{R}$ relates to the energy and entropy respectively.
- ii. The constant structure matrix $J = -J^T \in \mathbb{R}^n \times \mathbb{R}^n$.
- iii. $gu \in \mathbb{R}^n$ describes the interaction with the environment.

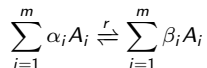
Energy balance and entropy balance with irreversible entropy creation.

$$\frac{dU}{dt} = \frac{\partial U}{\partial x}^T gu, \quad \frac{dS}{dt} = \sigma + \frac{\partial S}{\partial x}^T gu$$

Now we have two conjugated outputs, one with respect to the energy and another with respect to the entropy

$$y = g^T \frac{\partial U}{\partial x} \quad y_S = g^T \frac{\partial S}{\partial x}$$

A single chemical reaction



with α_i, β_i the stoichiometric coefficients for species A_i . **The mass balance** is

$$\dot{n}_i = r_i V + F_{ei} - F_{si} \quad i = 1, \dots, m$$

- n_i is the **number of moles** of the species i , $\mathbf{n} = (n_1, \dots, n_m)^\top$,
- $r_i = \bar{\nu}_i r$, where $r(\mathbf{n}, T) = (r_f - r_b)$ is the **reaction rate**
- $\bar{\nu}_i$ is the signed **stoichiometric coefficient**: $\bar{\nu}_i = \alpha_i - \beta_i$,
- F_{ei} and F_{si} are respectively the inlet and outlet **molar flows**, $\mathbf{F}_e = (F_{e1}, \dots, F_{em})^\top$
- The volume V in the reactor is assumed to be **constant** as well as the pressure

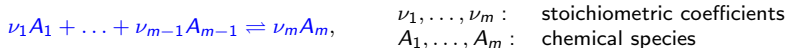
The mass balance can be represented as

$$\dot{\mathbf{n}} = C r V + \mathbf{F}_e - \mathbf{F}_i$$

where C is a $m \times 1$ is called the **stoichiometric vector**

The continuous stirred tank reactor (CSTR)

The chemical reaction is denoted by



together with the definition of the reaction rate:

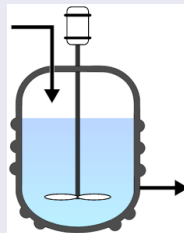
$$r(\mathcal{A}, T) = r_f(\mathcal{A}_f, T) - r_r(\mathcal{A}_f, T)$$

with \mathcal{A} the affinity of reaction.

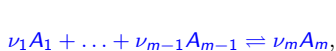
The mathematical model

The balance equations [Aris, 1989],

$$\underbrace{\dot{n}_i = r_i V + F_{ei} - F_{si}}_{\text{mass}}, \quad \underbrace{\dot{S} = \sum_{i=1}^m (F_{ei} s_{ei} - F_{si} s_i)}_{\text{entropy}} + \frac{Q}{T_w} + \sigma,$$



A single chemical reaction



ν_1, \dots, ν_m : stoichiometric coefficients
 A_1, \dots, A_m : chemical species
 \mathcal{A} : affinity of reaction

together with the definition of the reaction rate:

$$r(\mathcal{A}, T) = r_f(\mathcal{A}, T) - r_r(\mathcal{A}, T)$$

U = the internal energy

$$J = \underbrace{\begin{bmatrix} 0 & \dots & 0 & \bar{\nu}_1 \\ 0 & \dots & 0 & \vdots \\ 0 & \dots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \dots & -\bar{\nu}_m & 0 \end{bmatrix}}_{\text{stoichiometric matrix}},$$

$$\underbrace{g_1 = \begin{bmatrix} \mathbf{n}_e - \mathbf{n} \\ \phi \left(x, \frac{\partial U}{\partial x} \right) \end{bmatrix}}_{\text{Mass transfer}},$$

$$\underbrace{g_2 = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \frac{1}{T_e}}_{\text{Heat transfer}},$$

$$\begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} \frac{F}{V} \\ Q \end{bmatrix}$$

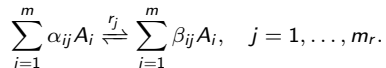
$$\{S, U\}_J = \mathcal{A} = - \sum_{i=1}^m \bar{\nu}_i \mu_i$$

$$\gamma = \frac{rV}{T\mathcal{A}} \geq 0,$$

μ_1, \dots, μ_m : chemical potentials
 rV : molar flow

Chemical reaction network

Consider a chemical reaction network involving m chemical species, among which m_r **chemical reactions**



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**:

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

where the $m \times m_r$ matrix \mathbf{C} is called the **stoichiometric matrix** and whose columns are the stoichiometric vectors of each reaction: $\mathbf{C} = [C_1, C_2, \dots, C_{m_r}]$, and $\mathbf{r} = [r_1, r_2, \dots, r_{m_r}]^T$ is the vector whose elements are the reaction rates of each individual reaction.

The **energy and entropy balance** are

$$\dot{U} = U_{in} - U_{out},$$

$$\dot{S} = S_{in} - S_{out} + \sigma$$

IPHS of chemical reaction networks

Consider the chemical reaction network

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

$$\dot{S} = \sigma + S_{in} - S_{out},$$

Define a vector containing the non-linear R_j functions of each reaction:

$$\mathbf{R} \in \mathbb{R}^{m_r} = [R_1, \dots, R_m]^\top,$$

then,

$$\dot{\mathbf{x}} = \underbrace{\begin{bmatrix} 0_m & \mathbf{C}\mathbf{R} \\ -\mathbf{R}^\top \mathbf{C}^\top & 0 \end{bmatrix}}_{J_R} \frac{\partial U}{\partial \mathbf{x}} + \begin{bmatrix} \mathbf{F}_e - \mathbf{F}_s \\ S_{in} - S_{out} \end{bmatrix}$$

The entropy balance is

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

where σ_i is the entropy production due to the i -th chemical reaction.

IPHS of chemical reaction networks

Alternatively,

The dynamic of the complete reaction is

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

Notice that

$$J_i = \begin{bmatrix} 0_m & C_i \\ -C_i^\top & 0 \end{bmatrix},$$

with C_i the $m \times 1$ stoichiometric vector.

A class of non-isothermal electrochemical processes

Electrochemical processes are characterized by chemical reactions that either produce or are produced by electrical energy. The reaction rates taking place at the electrodes are assumed to be described by the Butler-Vollmer kinetics.



where e^- are the electrons produced on the electrode. The reaction rate is

$$r = \frac{d\xi}{dt} = k_1^+ n_X e^{f_1 Fq/RTC} - k_1^- n_Y e^{(f_1-1)Fq/RTC}$$

The relation between the current I ; i.e. amount of charge transferred per second is

$$I = nF \frac{d\xi}{dt}$$

The electrochemical affinity of the reaction considering the electrostatic energy at the electrodes is

$$\tilde{\mathcal{A}} = \mu_X - [\mu_Y + \mu_{e^-}] + Fq/C$$

The charge on the electrode is

$$q = Fn_{e^-}$$

The entropy balance of the reaction

$$\frac{dS}{dt} = \frac{\tilde{\mathcal{A}}}{T} \frac{d\xi}{dt}$$

A class of non-isothermal electrochemical processes

Consider a simple electrochemical cell consisting of two compartments separated by a semipermeable membrane only permeable to the uncharged species Y, as depicted in figure 1.

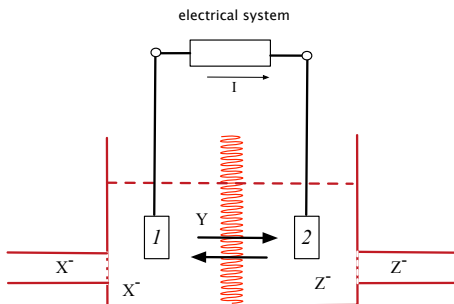


Figure: Electrochemical cell [Hjelmfelt et al., 1991]

The following reactions take part on the electrodes



A class of non-isothermal electrochemical processes

The chemical potentials of X^- and Z^- are kept constant at the values of the external reservoirs; i.e. these reservoirs act as ideal sources. Constant volume is constant, a well stirred cell and that the concentration of Y is uniform is assumed. Let C_1 and C_2 be the electrical capacitances of the electrodes.

$$r_1 = k_1^+ n_X e^{f_1 F q_1 / R T C_1} - k_1^- n_Y e^{(f_1 - 1) F q_1 / R T C_1}$$

$$r_2 = k_2^+ n_X e^{-f_2 F q_2 / R T C_1} - k_2^- n_Z e^{-(f_2 - 1) F q_2 / R T C_2}$$

and; therefore, the kinetic equations for the reactions on the electrodes are

$$\frac{d\xi_1}{dt} = r_1 \quad \frac{d\xi_2}{dt} = r_2$$

The molar balance equations for each species are

$$\begin{aligned} \frac{dn_{X^-}}{dt} &= -\frac{d\xi_1}{dt} \\ \frac{dn_Y}{dt} &= \frac{d\xi_1}{dt} - \frac{d\xi_2}{dt} \\ \frac{dn_{Z^-}}{dt} &= \frac{d\xi_2}{dt} \end{aligned}$$

We assume that the temperature of the system is uniform throughout and changes due to the electrochemical reactions. Hence, we assume that there are no changes in the heat capacity of the system, no phase changes and no heat transfer with the surroundings.

IPHS formulation of the chemical reaction scheme

The IPHS model of the purely chemical reaction of the electrochemical process is formulated as

$$\dot{\bar{x}} = \frac{1}{T} \begin{bmatrix} 0 & 0 & 0 & -r_1 \\ 0 & 0 & 0 & (r_1 - r_2) \\ 0 & 0 & 0 & r_2 \\ r_1 & -(r_1 - r_2) & -r_2 & 0 \end{bmatrix} \frac{\partial \bar{U}}{\partial \bar{x}}, \quad \frac{\partial \bar{U}}{\partial \bar{x}} = \begin{bmatrix} \mu_{X^-} \\ \mu_Y \\ \mu_{Z^-} \\ T \end{bmatrix}$$

with \bar{U} the energy of the chemical process without considering the electrical energy of the charge and $\bar{x} = [n_{X^-}, n_Y, n_{Z^-}, S]^T$. Splitting the model in two vector fields, each one related to a skewsymmetric structure matrix,

$$\dot{\bar{x}} = \frac{r_1}{T} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{bmatrix} \frac{\partial \bar{U}}{\partial \bar{x}} + \frac{r_2}{T} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \end{bmatrix} \frac{\partial \bar{U}}{\partial \bar{x}}$$

From this model we identify $R_1 = \frac{r_1}{T}$ and $R_2 = \frac{r_2}{T}$, one for each chemical reaction.

IPHS formulation of the electrochemical process

To formulate the IPHS model of the electrochemical process we shall now take into account the electrical part of the process. The evolution of the charge on the electrodes is given by [Hjelmfelt et al., 1991]

$$\begin{aligned}\frac{dq_1}{dt} &= F \frac{d\xi_1}{dt} - I \\ \frac{dq_2}{dt} &= F \frac{d\xi_2}{dt} + I\end{aligned}$$

where I is the current through the electrical load. Define $x = [n_Y, n_{X^-}, n_{Z^-}, q_1, q_2, S]$. The internal energy of the electrochemical process is given by the internal energy of the reaction and the electrical energy at the electrodes

$$U = \bar{U} + \left(\frac{1}{2} \frac{q_1^2}{C_1} - \frac{q_1 \mu_{e_1^-}}{F} \right) + \left(\frac{1}{2} \frac{q_2^2}{C_2} - \frac{q_2 \mu_{e_2^-}}{F} \right).$$

hence

$$\frac{\partial U}{\partial x} = \begin{bmatrix} \mu_Y, \\ \mu_{X^-}, \\ \mu_{Z^-}, \\ \frac{q_1}{C_1} - \frac{\mu_{e_1^-}}{F}, \\ \frac{q_2}{C_2} - \frac{\mu_{e_2^-}}{F} \end{bmatrix}.$$

IPHS formulation of the electrochemical process

Taken into account the electrical part we obtain

$$\dot{x} = \left(\frac{r_1}{T} J_1 + \frac{r_2}{T} J_2 \right) \frac{\partial U}{\partial x} + gI$$

with

$$J_1 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & F \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & -F & 0 & 0 \end{bmatrix}, \quad J_2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & F \\ 0 & 1 & -1 & 0 & -F & 0 \end{bmatrix}, \quad g = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix}$$

J_1 and J_2 maps the coupling between the electrical and chemical domain which is modulated by the Faraday's constant F . The thermodynamic driving forces of the process are now influenced by the electrical charge of the cell, indeed

$$\frac{\partial S^\top}{\partial x} J_1 \frac{\partial U}{\partial x} = \mu_{X^-} - \mu_{Y^-} - F \left(\frac{q_1}{C_1} - \frac{\mu_{e_1^-}}{F} \right) = \tilde{A}_1,$$

$$\frac{\partial S^\top}{\partial x} J_2 \frac{\partial U}{\partial x} = \mu_{Y^-} - \mu_{Z^-} - F \left(\frac{q_2}{C_2} - \frac{\mu_{e_2^-}}{F} \right) = \tilde{A}_2,$$

which correspond to the electrochemical affinities.

Ports and energy balance

The IPHS of the process has as input the current of the load, and the energy conjugated output of the system is

$$y = g^\top \frac{\partial U}{\partial x} = \left(\frac{q_2}{C_2} - \frac{\mu_{e_2}^{-o}}{F} \right) - \left(\frac{q_1}{C_1} - \frac{\mu_{e_1}^{-o}}{F} \right) = V_{12}$$

which is the voltage drop over the electrodes. At both electrodes, the chemical potential of the electrons at the vanishing potential is the same; i.e. $\mu_{e_1}^{-o} = \mu_{e_2}^{-o}$.

The energy balance of the process is

$$\frac{dU}{dt} = y^\top u = V_{12}I,$$

The entropy balance on the otherhand is given by

$$\frac{dS}{dt} = \sum_{i=1,2} \tilde{\gamma}_i \{S, U\}_{J_i}^2 + y_s v = \sum_{i=1,2} \sigma_i + \frac{V_{12}I}{T} = \sum_{i=1,2} \frac{\tilde{A}_i}{T} \frac{d\xi}{dt} + \frac{V_{12}I}{T}$$

Interconnection with a resistive load

The interconnection with an electrical load can be done through the port variables. For instance if a resistor with conductance ρ_r is connected, then the current is characterized by the following feedback

$$\begin{aligned} I &= -\rho_r V_{12} \\ &= -\rho_r y \\ &= -\rho_r \mathbf{g}^\top \frac{\partial U}{\partial \mathbf{x}} \end{aligned}$$

The evolution of the internal energy of the whole system is then described by

$$\begin{aligned} \frac{dU}{dt} &= -\frac{\partial U}{\partial \mathbf{x}}^\top \left(\rho_r \mathbf{g} \mathbf{g}^\top \right) \frac{\partial U}{\partial \mathbf{x}} \\ &= -\rho_r V_{12}^2 \end{aligned}$$

which corresponds to a dissipative IPHS. From a modelling perspective the interconnection of a thermodynamic system with an electrical system can be formulated as the interconnection of a reversible and an irreversible PHS.

$$\begin{aligned} \frac{dS}{dt} &= \sum_{i=1,2} \sigma_i - \frac{\rho_r}{T} V_{12}^2 \\ &= \sigma - \frac{\rho_r}{T} V_{12}^2. \end{aligned}$$

Some final remarks

- IPHS are thermodynamically coherent models which retain passivity features of PHS and satisfy the **second principle**.
- An irreversible port-Hamiltonian system (IPHS) formulation for a class of non-isothermal electrochemical process has been proposed.
- This model has a clear thermodynamic interpretation and since it is constructed in terms of internal energy and entropy conjugated ports it is straightforward to interconnect with other systems, such as electrical loads or sources.
- Future work will consider the interconnection of the proposed model with realistic loads, the study of more complex electrochemical reactions and the design of model based controllers.



Aris, R. (1989).

Elementary chemical reactor analysis.

Chemical Engineering, Butterworths, Stoneham, USA.



Eberard, D., Maschke, B. M., and van der Schaft, A. J. (2007).

An extension of Hamiltonian systems to the thermodynamic phase space: Towards a geometry of nonreversible processes.

Reports on Mathematical Physics, 60:175–198.



Favache, A. and Dochain, D. (2010).

Power-shaping control of reaction systems: The CSTR case.

Automatica, 46(11):1877 – 1883.



Grmela, M. and Öttinger, H. (1997).

Dynamics and thermodynamics of complex fluids. i. development of a general formalism.

Physical Review E, 56(6):6620–6632.



Hangos, K. M., Bokor, J., and Szederkényi, G. (2001).

Hamiltonian view on process systems.

AIChE Journal, 47:1819–1831.



Hjelmfelt, A., Schreiber, I., and Ross, J. (1991).

Efficiency of power production in simple nonlinear electrochemical systems.

J. Phys. Chem., 95:6048–6053.



Hoang, N., Couenne, F., Jallut, C., and Gorrec, Y. L. (2011).

The port hamiltonian approach to modeling and control of continuous stirred tank reactors.

Journal of Process Control, 21(10):1449–1458.



Maschke, B. and van der Schaft, A. (1992).

Port controlled Hamiltonian systems: modeling origins and system theoretic properties.

In *Proceedings of the 3rd IFAC Symposium on Nonlinear Control Systems, NOLCOS'92*, pages 282–288, Bordeaux, France.



Otero-Muras, I., Szederkényi, G., Alonso, A. A., and Hangos, K. M. (2008).

Local dissipative Hamiltonian description of reversible reaction networks.

Systems & Control Letters, 57:554–560.



van der Schaft, A. J. (2000).

L2-Gain and Passivity Techniques in Nonlinear Control.