Internal Entropy Production as a Lyapunov Function for Thermal Equilibrium in Irreversible Multiphase Systems

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Abstract: Thermodynamics has served as a framework to establish physics-based criteria for the stabilization, control and optimization of process systems. In this article, we establish conditions for the internal entropy production rate to characterize the stability properties of thermal equilibrium in irreversible multiphase systems. In particular, in Theorem 1, we show how, as a multiphase system evolves towards equilibrium, internal entropy production decreases monotonically in time for a particular class of multiphase systems. Being positive semi-definite and having a semi-negative definite time derivative, internal entropy production is thus a Lyapunov function that characterizes the stability of thermal equilibrium in multiphase irreversible systems.

Keywords: Non-equilibrium thermodynamics, Multiphase systems, Lyapunov stability, Internal entropy production

1. INTRODUCTION

Thermodynamic systems design, analysis, control and optimization stand as fundamental elements of process systems engineering. Chemical process systems are frequently assumed as quasi-stationary systems with state trajectories restrained to evolve inside a thermodynamic equilibrium manifold (Ydstie, 2016). In our research, we establish a methodology to characterize thermodynamic systems operating far from the equilibrium manifold. In this paper, we focus on developing a stability analysis for nonlinear multiphase processes that operate far from the equilibrium manifold. We investigate how thermodynamic-based criteria can be used to gain better understanding in dynamical process systems. Using the first and second laws of thermodynamics, we show that the internal entropy production rate can be used to design a physics-based Lyapunov function that characterizes the stability of an irreversible liquid-vapor systems as it evolves towards a thermodynamic equilibrium state.

Multiphase systems appear frequently in process engineering. Liquid-gas-solid operations in chemical and bio chemical-engineering (Seader et al., 2011), complex distillation separations (Drioli et al., 2015), and polymer crystallization (Sangroniz et al., 2021) are some examples where two or more phases interact as part of the process system. Despite its significance, the dynamic sta-

bility properties of chemical process systems is still not fully understood. Steady state multiplicity (Güttinger and Morari, 1999), and limit cycles (Lee et al., 1999) have been documented in process systems operations. A better understanding of the dynamical properties of multiphase systems should thus provide better design, control, and optimization methods for chemical process systems.

Physics-based formulations have been used to characterize the dynamical properties of process systems. Energy dissipation is, for instance, a stability criteria for nonlinear physical systems (Willems, 1972). Even though the early developments in dissipative analysis (Willems, 1972) are considered to be a cornerstone of modern analysis and applied control, the early applications of dissipative analysis were limited, for the most part, to the study of electro-mechanical systems. Dissipative theory applied to chemical processes received an increasing level of attention after its introduction during the late 1990s by Alonso and Ydstie (1996).

Thermodynamic potentials have well-defined convexity properties. In single-phase thermodynamic systems entropy is a concave function of the extensive variables (Callen, 1985), see Figure 1 (right). The concavity of entropy has allowed to assess for stability and to build control structures using Lyapunov theory and dissipative analysis (Favache and Dochain, 2009; García-Sandoval et al., 2015;
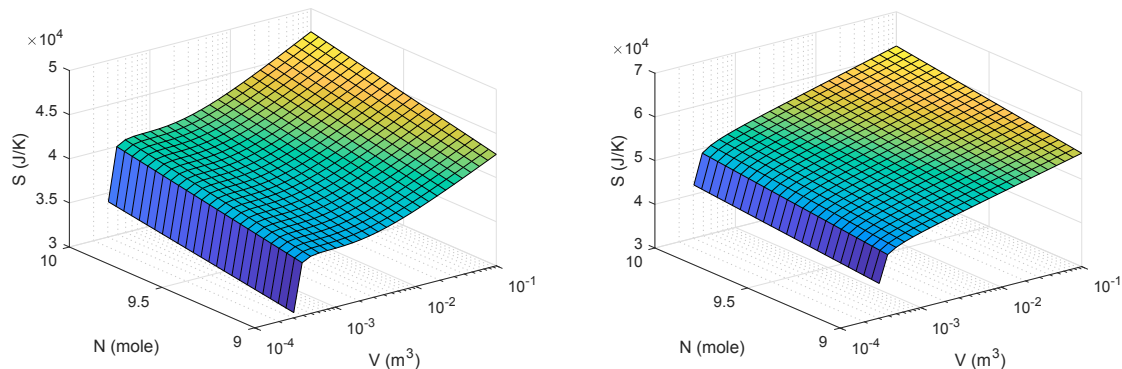
Fig. 1. Non-concave entropy for a liquid-vapor system (left) VS a concave entropy function in a gas system (right).

Hoang and Dochain, 2013). Unfortunately, the concavity of entropy is lost for multiphase systems (Callen, 1985), see Figure 1 (left). To characterize a system regardless of the convexity properties of its thermodynamic potentials, we propose to study multiphase chemical processes using an internal entropy production Lyapunov-based analysis.

Thermodynamic-based formulations have brought physical significance to the stability properties of reactive systems (Favache and Dochain, 2009; García-Sandoval et al., 2015) and have been used to establish control structures and to design observers based on irreversible thermodynamics (Hoang et al., 2012; Hoang and Dochain, 2019; Zárate-Navarro et al., 2022). Thermodynamic-based characterization of process systems is mostly limited to the study of single-phase systems. The work here presented sets the basis to extend physics-based characterization methodologies to multiphase systems.

In a previous paper we formulated a semi-positive definite entropy production equation $\dot{\Sigma}_i$ as a Lyapunov function candidate to characterize the stability properties in multiphase systems (Romo-Hernandez et al., 2019b). In this note we show that relaxation processes that occur as a system is driven towards thermodynamic equilibrium set the time derivative of $\dot{\Sigma}_i$ to be semi-negative definite. Following this property we state that $\dot{\Sigma}_i$ is a Lyapunov function to characterize the stability of equilibrium in irreversible multiphase systems.

The article is structured as follows. In Section 2 we use balance equations to set a mathematical model to describe an irreversible thermodynamic system that exchanges mass and energy with its environment. In Section 3 we extend the model to describe a multiphase system and we compute the entropy production rate for the system. In Section 4 we establish the internal entropy production function and we discuss how this function decreases in time as a consequence of relaxation processes that push an irreversible system towards equilibrium. We present concluding remarks in Section 5.

2. IRREVERSIBLE THERMODYNAMIC SYSTEMS

In this section we set the basis for the modeling of irreversible thermodynamic systems. Using molar and energy conservation principles, we establish a model to describe a macroscopic system that exchanges mass and energy with the environment.

Consider a lumped macroscopic system that exchanges mass and energy with its surroundings. An abstract representation of the system is depicted in Figure 2, left. The system has one mass convective inflow F_{in} and one mass convective outflow F_{out}. Additionally, the system exchanges mass at a rate J_{Nj} an energy at a rate J_E through non-convective transport mechanisms such as diffusive transport or chemical reactions. For modeling purposes we assume that:

1. The system is perfectly mixed.
2. Changes in potential, electromagnetic, and kinetic energy are negligible inside the system.
3. Work is done to (or done by) the system only as PdV work.
4. Crossed mass and energy diffusive transport mechanisms, such as thermodifussion or Dufour effect energy transfer, are negligible inside the system.
5. The system is locally at thermodynamic equilibrium.

As a consequence of assumptions 1-3, molar and energy holdups, N_j (moles) and U (J) respectively, can be described as

$$\frac{dN_j}{dt} = \dot{N}_{j,in} - \frac{N_j}{V}\dot{V} - J_{Nj}, \qquad j = 1, \ldots, c \quad (1)$$

$$\frac{dU}{dt} = \dot{H}_{in} - \left(\frac{U}{V} + P\right)\dot{V} + P\frac{dV}{dt} + \dot{Q} - J_E, \quad (2)$$

where $\dot{N}_{j,in}$ (moles/s) and $\dot{H}_{in}$ (W) represent molar and enthalpy convective inflows; V (m³) and P (Pa) refer to the volume and pressure of the system, respectively; $\dot{V}$ (m³/s) stands for the volumetric outflow rate of the convective outlet port F_{out}, see Figure 2, left; $\dot{Q}$ (W) is defined as a heat source; and the terms J_{Nj} (moles/s) and J_E (W) stand for non-convective outflow rates of moles and energy, respectively.

It is worth noticing that equations (1)-(2) describe a system where non-convective transport processes J_{Nj} and J_E play a role as a sinks of moles and energy. If non-convective transport processes worked as sources increasing the moles and energy of the system we must write a plus sign, instead of the minus, for the last terms in (1)-(2).

Considering differences in temperature and concentration between the blue and gray subsystems (Figure 2, left) as
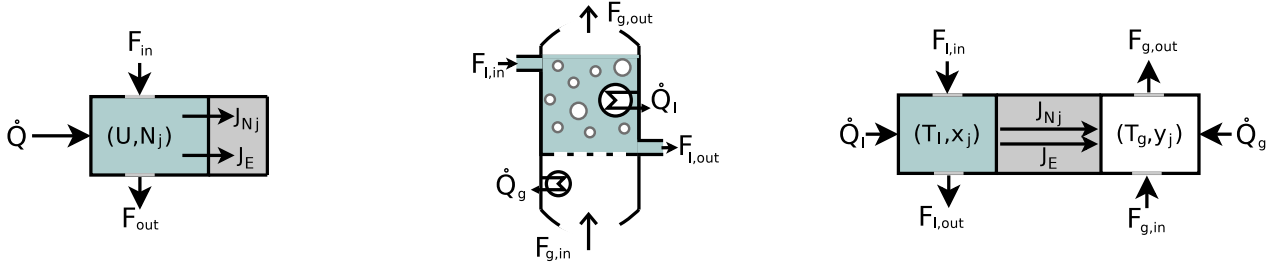
Fig. 2. Left: Lumped thermodynamic system that exchanges mass (F_{in}, F_{out}) and energy ($\dot{Q}$) with its surroundings, and where irreversible mechanisms transport mass (J_{Nj}) and energy (J_E). Center: Liquid-vapor open system. Right: Abstract representation of a liquid-vapor system as the interconnection of two lumped thermodynamic systems.

driving forces for mass and energy transfer mechanisms, we can establish the non-convective transport terms as (Bird et al., 2002; Taylor and Krishna, 1993)

$$J_{Nj} = k_j C(x_j - x_{j,i}) + x_j \sum_{k=1}^{c} J_{Nk} \qquad (3)$$

$$J_E = \lambda(T - T_i) + \sum_{k=1}^{c} h_j J_{Nk}, \qquad (4)$$

where k_j and λ stand for mass and energy transport coefficients; C, x_j, and T represent the total concentration, molar fraction of component j and temperature of blue subsystem, respectively; whereas $x_{j,i}$ and T_i stand for the molar fraction of j and the temperature of the gray subsystem; finally h_j in the last term of the energy balance stands for the partial molar enthalpy of component j in the blue system. No crossed mass or energy transport effects are considered in (3)-(4) as a consequence of assumption 4.

It is worth noting that the balance equations (1)-(4) are written in terms of extensive variables whereas the transport equations (3)-(4) are written in terms of intensive variables. To write both the balance and the transport equations in terms of intensive variables we use the following change of thermodynamic coordinates

$$N_j = x_j \sum_{k=1}^{c} N_k, \quad U = U_0 + C_v(T - T_o) \sum_{k=1}^{c} N_k \quad (5)$$

to rewrite (1)-(4). The first step to write the system's model in terms of intensive variables is to differentiate (5) with respect to time to obtain

$$N\frac{dx_j}{dt} = \frac{dN_j}{dt} - x_j \frac{dN}{dt}, \qquad j = 1, \dots, c - 1 \qquad (6)$$

$$NC_v \frac{dT}{dt} = \frac{dU}{dt} - C_v(T - T_0)\frac{dN}{dt}, \qquad (7)$$

where, the sake of simplicity, we have writen $N = \sum_{k=1}^{c} N_k$ to represent the total molar holdup of the system. After some tedious algebra, substitution of (1)-(2) into (6)-(7) leads to

$$CV\frac{dx_j}{dt} = \dot{N}_{j,in}(x_{j,in} - x_j) - j_{Nj}, \quad j = 1, \dots, c - 1 \quad (8)$$

$$CV\frac{dT}{dt} = \dot{N}_{j,in}C_{v,in}(T_{in} - T)$$
$$+ P_{in}\dot{V}_{in} - PV - P\frac{dV}{dt} - j_E, \qquad (9)$$

where C_v represents the isochoric heat capacity of the fluid in the blue subsystem, and

$$j_{Nj} = k_j C(x_j - x_{j,i}) \qquad (10)$$

$$j_E = \lambda(T - T_i) + \frac{P}{C}\sum_{k=1}^{c} J_{Nk} \qquad (11)$$

stand for adjusted non-convective transport terms. It is worth remarking that, as a consequence of the coordinate change, the advective terms

$$x_j \sum_{k=1}^{c} J_{Nk} \text{ and } \sum_{k=1}^{c} h_j J_{Nk}$$

in the transport equations (3)-(4) no longer appear as part of the system description (8)-(11). The dynamical behavior of the system, described in terms of intensive variables, no longer requires an explicit description of advective transport.

Even tough the system of interest (composite blue-gray system depicted in Figure 2, left) does not necessarily have homogeneous temperature or composition, the change of coordinates 5 is still considered valid as the system is locally at thermodynamic equilibrium, assumption 5.

In the following section we use the modeling framework described in this section to establish an abstract description of a multiphase system. Using the established model we set a function that describes how entropy is produced as a consequence of internal transport mechanisms that occur inside an irreversible system.

3. INTERNAL ENTROPY PRODUCTION IN A MULTIPHASE SYSTEM

A multiphase system can be understood as the coupling of two bulk phases through an interface subsystem. In Figure 2, center, we represent a liquid-vapor open system that exchanges mass and energy with its surroundings. In Figure 1, right, we represent the liquid-vapor open system as the interconnection of two lumped macroscopic systems.

Temperature and composition of the liquid system is represented as the pair [1] (T_l, x_j) whereas for the vapor system we set temperature and composition as (T_g, y_j). The dynamic model (8)-(9) can be easily extended to describe the temperature and composition of a liquid-vapor system as

$$C_l V_l \frac{dx_j}{dt} = \dot{N}_{j,in,l}(x_{j,in} - x_j) - j_{Nj,l}, \qquad (12)$$

$$C_g V_g \frac{dy_j}{dt} = \dot{N}_{j,in,g}(y_{j,in} - y_j) + j_{Nj,g}, \qquad (13)$$

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[1] Saying that (T, x_j) is a pair or referring to $(T_i, x_{j,i}, y_{j,i})$ as a triplet is an abuse of notation. Strictly speaking, we should be talking about a $(c+1)$−tuple $(T, x_1, \dots, x_c)$ to represent the temperature and composition of a bulk-phase or a $(2c+1)$−tuple $(T, x_1, \dots, x_c, , y_1, \dots, y_c)$ to represent the temperature and composition of the interface.
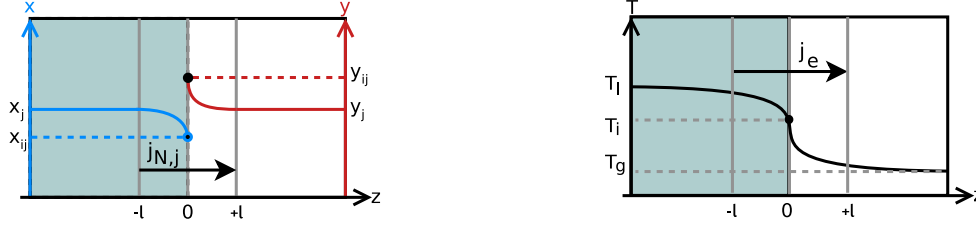
Fig. 3. Composition variations between liquid (blue), interface, and vapor (white) subsystems inside an irreversible multiphase system (left). Monotonic decrease of temperature between liquid (blue), interface, and vapor (white) subsystems inside an irreversible multiphase system (right)

$$C_l V_l \frac{dT_l}{dt} = \dot{N}_{j,\mathrm{in},l} C_{v,\mathrm{in},l}(T_{\mathrm{in},l} - T_l)$$
$$+ P_{\mathrm{in},l}\dot{V}_{\mathrm{in},l} - P_l V_l - P\frac{dV_l}{dt} - j_{E,l}, \quad (14)$$

$$C_g V_g \frac{dT_g}{dt} = \dot{N}_{j,\mathrm{in},g} C_{v,\mathrm{in},g}(T_{\mathrm{in},g} - T_g)$$
$$+ P_{\mathrm{in},g}\dot{V}_{\mathrm{in},g} - P_g V_g - P\frac{dV_g}{dt} + j_{E,g}, \quad (15)$$

where subscripts l and g refer a variable to the liquid or vapor subsystem, and the index of the molar balances (12)-(13) runs as $j = 1, \ldots, c-1$.

Between phases, there exists an interface that interconnects liquid and vapor subsystems. Temperature and composition of the interface are represented as the triplet [1] $(T_i, x_{j,i}, y_{j,i})$. Far from thermodynamic equilibrium, temperatures and compositions may vary between the bulk-phases and the interface subsystem as depicted in Figure 3. As a consequence of temperature and composition variations in a multiphase system, transport processes occur between the bulk-phases and the interface. Transport processes between the liquid phase and the interface can be described using equations (3)-(4). An equivalent formulation can be made to describe the transport between the vapor phase and the interface. Assuming that the interface dynamics is faster than the bulk-phase dynamics we can consider that neither mass nor energy accumulate in the interface, thus

$$k_{j,l}C_l(x_j - x_{j,i}) - k_{j,g}C_g(y_{j,i} - y_j) + (x_j - y_j)J_N = 0 \quad (16)$$

$$\lambda_l(T_l - T_i) - \lambda_g(T_i - T_g)$$
$$+ \sum_{k=1}^{c}(h_{j,l} - h_{j,g})J_{Nk} = 0 \quad (17)$$

where the sub-index j runs as $j = 1, \ldots, c-1$ in equation (16), and $J_N = \sum_{k=1}^{c} J_{Nk}$ stands as the total molar transport rate through the interface. As the interface is locally at thermodynamic equilibrium (Taylor and Krishna, 1993), the liquid-vapor system description is completed with local liquid-vapor equilibrium and sum relations

$$y_{j,i} - K_{j,i}x_{j,i} = 0 \qquad j = 1, \ldots, c \qquad (18)$$
$$1 - \sum_{k=1}^{c} x_{k,i} = 0 \qquad (19)$$
$$1 - \sum_{k=1}^{c} y_{k,i} = 0 \qquad (20)$$

where $K_{j,i}$ stands for the liquid-vapor thermodynamic equilibrium $K-$value of component j evaluated at the interface conditions.

Equations (12)-(20) stand as a differential algebraic system with $4c + 4$ equations that, once solved, gives time dependent trajectories for the state

$$(T_l, T_g, T_i, x_j, y_j, x_{j,i}, y_{j,i}, J_N), \qquad j = 1, \ldots, c.$$

The second law of thermodynamics establishes that as mass and energy are transferred between the phases and the interface of the composite system, entropy increases at a rate $\dot{S}_{\mathrm{gen}} \geq 0$. We call this rate the entropy production of the system. To quantify the entropy production rate, we require to couple an entropy balance over the liquid-vapor system together with the entropy fundamental equation. Both the entropy balance and the entropy fundamental equation are briefly presented below.

An entropy balance (Sandler, 1999) over the liquid-vapor system depicted in Figure 2, right, allows to write the internal entropy production rate as

$$\dot{S}_{\mathrm{gen}} = \dot{S}_{\mathrm{out}} - \dot{S}_{\mathrm{in}} + \frac{dS}{dt} - \sum_{p \in \{l,g\}} \frac{\dot{Q}_p}{T_{Q,p}}. \qquad (21)$$

where $\dot{S}_{\mathrm{in}}$ (W/K) and $\dot{S}_{\mathrm{out}}$ (W/K) stand for entropy inflow and outflow rates that come as a consequence of the system exchanging mass with the environment, and $T_{Q,p}$ represents the temperature at which the heat input Q_p is delivered to phase p. Note that for the liquid-vapor system, the entropy flow-rates can be described as

$$\dot{S}_{\mathrm{in}} = \sum_{j=1}^{c}(\dot{N}_j s_j)|_{\mathrm{in},l} + \sum_{j=1}^{c}(\dot{N}_j s_j)|_{\mathrm{in},g} \qquad (22)$$
$$\dot{S}_{\mathrm{out}} = \sum_{j=1}^{c}(\dot{N}_j s_j)|_{\mathrm{out},l} + \sum_{j=1}^{c}(\dot{N}_j s_j)|_{\mathrm{out},g} \qquad (23)$$

where s_j stands for the liquid, or vapor, partial molar entropy of component j at the inflow (outflow) conditions.

Entropy is a function that depends on the energy, volume, and molar holdups of a physical system (Callen, 1985). Differentiation of the relation $S = S(U, V, N_j)$ leads to the entropy fundamental relation (Callen, 1985)

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{k=1}^{c} \frac{\mu_k}{T}dN_j.$$

Entropy is an extensive property. Using the fundamental relation we can therefore write entropy variations in time inside a liquid-vapor system as

$$\frac{dS}{dt} = \frac{dS_l}{dt} + \frac{dS_g}{dt}$$
$$= \sum_{p \in \{l,g\}} \left(\frac{1}{T_p}\frac{dU_p}{dt} + \frac{P_p}{T_p}\frac{dV_p}{dt} - \sum_{k=1}^{c} \frac{\mu_{k,p}}{T_p}\frac{dN_{k,p}}{dt} \right). \qquad (24)$$

Substitution of molar and energy balances (1)-(2) in the fundamental relation (24), and combining (24) with (21) gives

$$\dot{S}_{\text{gen}} = \left\{ \begin{array}{c} \text{Environment} \\ \text{Interaction} \\ \text{terms} \end{array} \right\} + \left(\frac{1}{T_g} - \frac{1}{T_l} \right) J_E$$
$$+ \sum_{k=1}^{c} \left(\frac{\mu_{k,g}}{T_g} - \frac{\mu_{k,l}}{T_l} \right) J_{Nk}, \quad (25)$$

where

$$\left\{ \begin{array}{c} \text{Environment} \\ \text{interaction} \\ \text{terms} \end{array} \right\} = \dot{S}_{\text{out}} - \dot{S}_{\text{in}} + \sum_{p \in \{l,g\}} \left\{ \left(\frac{1}{T_p} - \frac{1}{T_{Q,p}} \right) \dot{Q}_p \right.$$
$$\left. + \frac{1}{T_p} \left(\dot{H}_{\text{in},p} - \frac{H_p}{V_p} \dot{V}_p \right) - \sum_{k=1}^{c} \frac{\mu_{k,p}}{T_p} \left(\dot{N}_{\text{in},p} - \frac{N_p}{V_p} \dot{V}_p \right) \right\}$$

stands for the entropy produced as the system exchanges mass and energy with the surroundings.

4. ENTROPY PRODUCTION-BASED LYAPUNOV FUNCTION

As we are interested in characterizing the entropy production due to interface transport mechanisms, we define the internal entropy production for the liquid-vapor system as a bi-linear form on fluxes J_i and driving forces X_i

$$\dot{\Sigma}_i := \dot{S}_{\text{gen}} - \left\{ \begin{array}{c} \text{Environment} \\ \text{Interaction} \\ \text{terms} \end{array} \right\} = \sum_{i \in \{N_j, E\}} J_i X_i \quad (26)$$

where J_{Nj}, $j = 1, \ldots, c$, and J_E stand for interface fluxes of moles and energy, respectively, see (3)-(4); and

$$X_{Nk} = \left(\frac{\mu_{k,g}}{T_g} - \frac{\mu_{k,l}}{T_l} \right), \qquad j = 1, \ldots, c \quad (27)$$

$$X_E = \left(\frac{1}{T_g} - \frac{1}{T_l} \right) \quad (28)$$

represent driving forces for moles and energy transport through the interface of the liquid-vapor system.

4.1 Change of thermodynamic coordinates

As chemical potential is a state variable that is difficult to measure, we rewrite the internal entropy production in terms of alternative fluxes and forces as

$$\dot{\Sigma}_i = \sum_{i \in \{N_j, E\}} J_i' X_i' \quad (29)$$

where (Romo-Hernandez et al., 2019b)

$$J_{Nj}' = R J_{Nj}, \qquad X_{Nj}' = \ln y_j^\star - \ln y_j, \quad j = 1, \ldots, c,$$
$$J_E' = \lambda_l (T_l - T_i), \qquad X_E' = \left(\frac{1}{T_g} - \frac{1}{T_l} \right).$$

In the definition of the alternative fluxes and forces for the internal entropy production, Equation (30), R stands for the ideal gas constant and $y_j^\star$ represents the vapor composition of component j that is in thermodynamic equilibrium with the liquid [2].

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[2] Assuming that we wish to describe a low pressure system at pressure P where the vapor phase can be considered as an ideal gas mixture, we can describe the vapor equilibrium composition using Raoult's modified liquid-vapor K-values as (Seader et al., 2011)

$$y_j^\star = K_j x_j, \qquad K_j = \gamma_j \frac{P_j^{\text{sat}}}{P} \qquad j = 1, \ldots, c,$$

where the activity coefficient γ_j and the saturation pressure are computed using the liquid bulk-phase composition and temperature.

4.2 Time decreasing properties of $d\dot{\Sigma}_i/dt$

The internal entropy production is a function that depends on the temperatures, compositions, and transport terms inside a non-equilibrium multiphase system. To show that the internal entropy production is a Lyapunov function that characterizes the stability of thermodynamic equilibrium, it has been demonstrated that there exists a domain Ω that contains the thermodynamic equilibrium state $z^\star$ such that (Romo-Hernandez et al., 2019b)

$$\dot{\Sigma}_i(z) > 0, \qquad z \neq z^\star, \ z \in \Omega \quad (30)$$
$$\dot{\Sigma}_i(z) = 0, \qquad z = z^\star \quad (31)$$

where

$$z = (T_l, T_g, T_i, x_j, y_j, x_{j,i}, y_{j,i}, J_N), \quad j = 1, \ldots, c.$$

A second condition required for $\dot{\Sigma}_i$ to be a Lyapunov function is that $d\dot{\Sigma}_i/dt$ is negative semi-definite far from thermodynamic equilibrium. In the theorem presented below we tackle the problem of showing that energy-related relaxation processes decrease the internal entropy production $\dot{\Sigma}_i$ in time inside a multiphase system. Therefore showing that $\dot{\Sigma}_i$ behaves, under certain restrictions, as a Lyapunov function that characterizes the evolution of a system towards thermodynamic equilibrium.

Theorem 1. Consider a multiphase system where temperature between phases changes monotonically [3] between phases and assume that the system is at chemical equilibrium, that is

$$y_j = y_{j,i}, \qquad x_{j,i} = x_j, \qquad y_j = K_j x_j \qquad j = 1, \ldots, c.$$

Assume that relaxation processes drive the system towards the thermodynamic equilibrium state, that is, temperature changes in time tending to the equilibrium temperature $T^\star$

$$T_l \to T^\star, \quad T_g \to T^\star, \quad , T_i \to T^\star.$$

Then, the internal entropy production satisfies

$$\frac{d\dot{\Sigma}_i}{dt} < 0 \quad \text{for } T_l \neq T_g \neq T_i \quad (32)$$

$$\frac{d\dot{\Sigma}_i}{dt} = 0 \quad \text{at equilibrium } T_l = T_g = T_i \quad (33)$$

Dem: Without loss of generality we will consider the case shown in Figure 3, right, when [4] $T_l > T_i > T_g$. As the system is at chemical equilibrium, the internal entropy production function is reduced to

$$\dot{\Sigma}_i = \left(\frac{1}{T_g} - \frac{1}{T_l} \right) \dot{Q}_i \quad (34)$$

where $\dot{Q}_i = \lambda_l (T_l - T_i)$ stands for the heat transferred between the liquid bulk-phase and the interface. Computing the time derivative of (35) we obtain

$$\frac{d\dot{\Sigma}_i}{dt} = \dot{Q}_i \left(\frac{1}{T_l^2} \frac{dT_l}{dt} - \frac{1}{T_g^2} \frac{dT_g}{dt} \right) + \frac{d\dot{Q}_i}{dt} \left(\frac{T_l - T_g}{T_l T_g} \right) \quad (35)$$

As $T_l > T_i > T_g$, it follows immediately that $\dot{Q}_i = \lambda_l (T_l - T_i) > 0$ and that $T_l - T_g > 0$. Additionally, as the relaxation processes occur, the liquid temperature will decrease to an equilibrium value $T_l \to T^\star$ and the

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[3] Monotonicity of temperature implies that heat is neither accumulated nor generated inside the liquid-vapor interface.

[4] This demonstration works also for the case when $T_g > T_i > T_l$ as long as the temperature variations across phases are monotonic.

vapor temperature will increase to an equilibrium value $T_g \to T^\star$. As relaxation processes decrease temperature differences between phases, the heat transfer $\dot{Q}_i$ decreases in time. Thus, relaxation processes bound derivatives of temperature and heat transfer as

$$dT_l/dt < 0 < dT_g/dt, \quad dQ_i/dt < 0.$$

It follows immediately from the previous inequalities that

$$d\dot{\Sigma}_i/dt < 0$$

as relaxation processes push temperatures towards thermal equilibrium. It is easy to verify that (36) reaches zero at the thermal equilibrium state $T_l = T_g = T_i = T^\star$. $\square$

5. CONCLUSIONS AND FUTURE WORK

The thermodynamic characterization of irreversible processes here presented had brought to light phenomenological insights on the dynamic characteristics of multiphase systems. In Theorem 1, we have presented formal evidence showing that internal entropy production, Equation (27), decreases in time when multiphase systems evolve towards thermal equilibrium. Internal entropy production is thus a Lyapunov function that characterizes the stability of nonisothermal multiphase systems. An extension of Theorem 1 is still required to consider the stabilization effects of mass transport relaxation processes in multiphase systems. Even thought the main result in this article is restricted to system with thermal energy transport, we strongly believe that the methodology here presented can be extended to show that internal entropy production $\dot{\Sigma}_i$ decreases in time in systems with interface molar/mass transport processes.

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REFERENCES

Alonso, A.A. and Ydstie, B.E. (1996). Process systems, passivity and the second law of thermodynamics. *Computers and Chemical Engineering, Special Issue on the European Symposium on Computer Aided Process Engineering (ESCAPE-6)*, 20(Supplement 2), S1119–S1124.

Antelo, L.T., Otero-Muras, I., Banga, J.R., and Alonso, A.A. (2007). A systematic approach to plant-wide control based on thermodynamics. *Computers and Chemical Engineering*, 31(5-6), 677–691.

Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (2002). *Transport Phenomena*. John Wiley & Sons, New York, 2nd edition.

Callen, H.B. (1985). *Thermodynamics and an Introduction to Thermostatistics*. John Wiley & Sons, New York, 2nd edition.

Drioli, E., A.Ali, and Macedonio, F. (2015). Membrane distillation: Recent developments and perspectives. *Desalination*, 356, 56–84. State-of-the-Art Reviews in Desalination.

Favache, A. and Dochain, D. (2009). Thermodynamics and chemical systems stability: The CSTR case study revisited. *Journal of Process Control*, 19(3), 371–379.

García-Sandoval, J.P., González-Álvarez, V., and Calderón, C. (2015). Stability analysis and passivity properties for a class of chemical reactors: Internal entropy production approach. *Computers and Chemical Engineering*, 75, 184–195.

Güttinger, T.E. and Morari, M. (1999). Predicting multiple steady states in equilibrium reactive distillation. 1. analysis of nonhybrid systems. *Industrial & Engineering Chemistry Research*, 38(4), 1633–1648.

Hoang, H., Couenne, F., Jallut, C., and Le Gorrec, Y. (2012). Lyapunov-based control of non isothermal continuous stirred tank reactors using irreversible thermodynamics. *Journal of Process Control*, 22(2), 412–422.

Hoang, N.H. and Dochain, D. (2013). On an evolution criterion of homogeneous multi-component mixtures with chemical transformation. *Systems and Control Letters*, 62(2), 170–177.

Hoang, N. and Dochain, D. (2019). A comment on thermodynamically consistent feasibility condition of asymptotic observers. *Chemical Engineering Science*, 199, 258–274.

Lee, M., Dorn, C., Meski, G.A., and Morari, M. (1999). Limit cycles in homogeneous azeotropic distillation. *Industrial & Engineering Chemistry Research*, 38(5), 2021–2027.

Romo-Hernandez, A., Hudon, N., E. Ydstie, B., and Dochain, D. (2019a). A non-equilibrium approach to model flash dynamics with interface transport. *Journal of Process Control*, 80, 211–222.

Romo-Hernandez, A., Hudon, N., Ydstie, B., and Dochain, D. (2019b). On the positivity of entropy production in multiphase thermodynamic systems. *IFAC-PapersOnLine*, 52(7), 13–18.

Romo-Hernandez, A., Hudon, N., Ydstie, B.E., and Dochain, D. (2019). A non-equilibrium approach to model flash dynamics with interface transport. *arXiv e-prints*, arXiv:1902.05445.

Sandler, S.I. (1999). *Chemical and Engineering Thermodynamics*. Wiley, New York, 3rd edition.

Sangroniz, L., Wang, B., Su, Y., Liu, G., Cavallo, D., Wang, D., and Müller, A. (2021). Fractionated crystallization in semicrystalline polymers. *Progress in Polymer Science*, 115, 1–40.

Seader, J.D., Henley, E.J., and Roper, D.K. (2011). *Separation Process Principles*. Wiley, New York, third edition.

Taylor, R. and Krishna, R. (1993). *Multicomponent Mass Transfer*. Wiley & Sons, Inc., New York, 1st edition.

Willems, J.C. (1972). Dissipative dynamical systems part I: General theory. *Archive for Rational Mechanics and Analysis*, 45(5), 321–351.

Ydstie, B.E. (2016). Stability of multi-phase systems evolving on an equilibrium manifold. *IFAC-PapersOnLine*, 49(7), 943–948. 11th IFAC Symposium on Dynamics and Control of Process Systems Including Biosystems DYCOPS-CAB 2016.

Zárate-Navarro, M., Dubljevic, S., Campos-Rodríguez, A., Aguilar-Garnica, E., and García-Sandoval, J. (2022). Dissipative boundary control for an adiabatic plug flow reactor with mass recycle. *IEEE Access*, 10, 30939–30948.