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A non-equilibrium approach to model flash dynamics with interface transport

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ABSTRACT

In this paper, we present a modeling framework for a class of multiphase chemical systems based on non-equilibrium thermodynamics. Compartmental modeling is used to establish the dynamic properties of liquid–vapor systems operating far from thermodynamic equilibrium. In addition to the bulk-phase molar/energetic dynamics, interface transport processes yield to algebraic constraints in the model description. The irreversible system is thus written as a system of differential-algebraic equations (DAEs). The non-equilibrium liquid–vapor DAE system is shown to be of index one. A local stability analysis for the model shows that the equilibrium state is unstable for non-isobaric operation regimes, whereas numerical evidence shows that isobaric operation regimes are stable. To extend the stability analysis, internal entropy production for the irreversible flash-drum is presented as a Lyapunov function candidate.

1. Introduction

Despite its historical and contemporary significance, design, control and operation of multiphase processes have been challenging tasks in process systems engineering over the years [1,2]. In this paper, we explore the possibility of modeling a special class of multiphase systems, namely the open flash-drum, utilizing a non-equilibrium physics-based perspective. In contrast with traditional equilibrium formulations, non-equilibrium models can keep track of irreversible phenomena such as energy degradation and entropy production [3]. Moreover, irreversible schemes have led to useful insights for stability analysis and feedback control design in the chemical process engineering literature [4–8]. The work presented in this paper expands the available modeling techniques and stability theory to include open liquid–vapor systems that operate far from thermodynamic equilibrium.

Dissipative systems theory, originally proposed by Willems Willems [9] as an extension of (linear) passivity-based analysis, is considered as a fundamental tool for the analysis and control design of mechanical and electrical systems. Chemical dissipative systems theory has received an increasing level of attention after Alonso and Ydstie [4,5] developed the theory in detail using the first and second laws of thermodynamics. Thermodynamic potentials have proven to be useful for the design of plant-wide control structures as shown in [10]. In the paper by Favache and Dochain [6], the possibility of characterizing the continuous stirred tank reactor (CSTR) through energetic and entropic formulations is explored with insightful results. In the work by Hoang et al. [11] Lyapunov control laws, based on thermodynamic availability, are developed for a larger class of non equilibrium CSTRs. In the paper by García-Sandoval et al. [7] the dissipative properties for irreversible CSTRs are determined based on an internal entropy production approach.

Thermodynamic process systems theory has focused mostly on single-phase systems, also known as simple thermodynamic systems. And it is not until recently that thermodynamic multiphase systems theory has gained an increasing interest from the scientific community.

For simple thermodynamic systems, entropy (resp. internal energy) is a strictly concave (resp. convex) function of the extensive variables [12], as depicted Fig. 1 (right). Such concavity properties had permitted to assess the stability of thermodynamic systems by using Lyapunov theory and dissipative analysis [6,7,11]. For multiphase systems the concavity is not strict [13] as the very existence of separate phases follows as a consequence of the loss of concavity in entropy [12], see Fig. 1 (left). To characterize a system regardless

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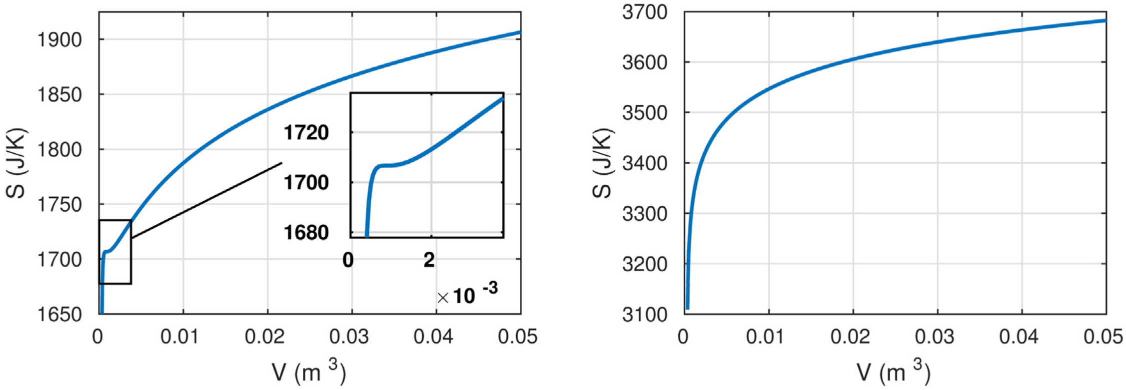

Fig. 1. Van der Waals entropy for water: liquid–vapor (left) and gas (right).

of its convexity properties, we propose to study liquid–vapor processes based on internal entropy production rather than entropy or internal energy potentials.

Historically, systems theory analysis for multiphase processes can be traced back to the pioneering work of Rosenbrock [14]. Rosenbrock [14] demonstrated that a non-ideal binary distillation column operates at a unique asymptotically stable steady state. Three decades later, Rouchon and Creff [15] developed a stability analysis, based on geometric considerations, for a multicomponent flash-drum. The approach proposed by Rouchon and Creff [15] unfortunately does not extend to multistage process units. In a more recent contribution, Ydstie [8] developed conditions for the existence of a unique stable steady-state for an adiabatic flash-drum operating on an equilibrium manifold. Looking forward to extend process systems theory to include dynamical non-equilibrium liquid–vapor units, a modeling framework is presented in a previous contribution by Romo-Hernandez et al. [16]. The present paper serves as an extension to [16] that includes the derivation of the entropy production function for the irreversible flash-drum. Following the contribution by García-Sandoval et al. [7], entropy production can serve as a Lyapunov function candidate to characterize the dynamic properties for nonlinear irreversible flash-drums. In addition, details on mathematical procedures excluded from [16] are included in the present paper.

The paper is organized as follows. In Section 2, the non-equilibrium liquid–vapor model is derived as a system of differential-algebraic equations (DAEs) from mass and energy conservation principles. The DAE model takes into account exchange processes through the interface, viewed as constraints on the dynamics of the system. In Section 3, internal entropy production for the flash-drum is written as the sum of products of flows and driving forces. Being positive definite, internal entropy production is a physics-based Lyapunov function candidate to characterize the stability of the irreversible flash-drum. Numerical results are presented in Section 4. First, the DAE model is rewritten and improved for numerical integration using a bijective change of coordinates. Second, a non-ideal water-methanol liquid gas mixture is considered to represent dynamical trajectories. Results regarding Lyapunov's first and second methods for stability of the water-methanol system are presented. Conclusions and future areas for research are discussed in Section 5.

2. Liquid–vapor thermodynamic systems

In this section, we develop a system of nonlinear differential-algebraic equations (DAEs) of index one that describes a flash-drum as the interconnection of two thermodynamic subsystems. We motivate the need for such description through Gibbs equation as a way to describe entropy variations inside an open liquid–vapor system. The obtained DAE model is an abstract representation of the first law of thermodynamics applied to the irreversible flash-drum.

A thermodynamic system is completely defined once its physical properties are determined. For instance, all the physical properties of a closed chemical system with c chemical components can be recovered once a particular set of coordinates (U, V, N_1, ..., N_c) is known. Such coordinates represent the internal energy, volume, and mole numbers of the system, respectively. This is known as the first postulate of thermodynamics and it was proposed by Callen [12], on the basis of the Gibbs' school on modern thermodynamics.

The second postulate of thermodynamics defines the entropy as a function that is maximized at thermodynamic equilibrium [12]. Moreover, such function is related to the intensive variables [17].

Definition 1 *(Entropy).* Let U (J), V (m^3), and N_j (mol), $j \in \{1, \ldots, c\}$, represent the internal the internal energy, volume, and mole numbers for a closed thermodynamic system. Entropy is a concave function

$$S = S(U, V, N_1, \ldots, N_c) \tag{1a}$$

that is maximized over the equilibrium states of the thermodynamic system. The function S(·) is said to be homogeneous of degree one, *i.e.*:

$$S(\lambda U, \lambda V, \lambda N_1, \ldots, \lambda N_c) = \lambda S(U, V, N_1, \ldots, N_c), \forall \lambda > 0.$$

Entropy is at least once differentiable. The derivatives of S(·) satisfy

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \frac{\partial S}{\partial V} = \frac{P}{T}, \frac{\partial S}{\partial N_j} = \frac{-\mu_j}{T}, \quad j \in \{1, \ldots, c\}. \tag{1b}$$

where T (K), P (Pa), μ_j (J/mol), $j = \in \{1, \ldots, c\}$, stand for the temperature, pressure and chemical potential, respectively. As a consequence of (1b), the intensive variable coordinates (T, P, μ_1, ..., μ_c) are said to be the conjugates to the extensive variables (U, V, N_1, ..., N_c). □

The formal structure of thermodynamics, Eq. (1), is defined for closed systems at thermodynamic equilibrium [12]. Nevertheless Eq. (1) is still considered valid locally when studying systems that are not at thermodynamic equilibrium [11]. Non-homogeneous systems, non-stationary processes, and open vessels exchanging mass and energy with the environment are some examples of non-equilibrium systems. Computing the differential of (1a) gives Gibbs equation

$$dS = \frac{1}{T}dU + \frac{P}{T}dV + \frac{\mu_1}{T}dN_1 + \ldots + \frac{\mu_c}{T}dN_c. \tag{2}$$

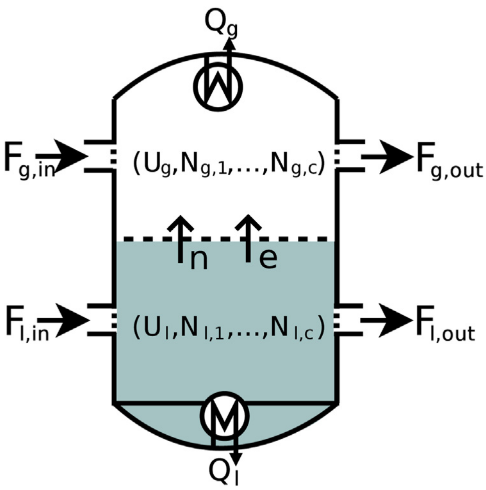

Fig. 2. Liquid–vapor open thermodynamic system with interface transport.

When time derivatives are considered instead of the differentials in (2) we get

$$\frac{dS}{dt}=\frac{1}{T}\frac{dU}{dt}+\frac{P}{T}\frac{dV}{dt}+\frac{\mu_1}{T}\frac{dN_1}{dt}+\ldots+\frac{\mu_c}{T}\frac{dN_c}{dt}. \tag{3}$$

As the derivatives on the right hand side of (3) represent time variations of macroscopic variables, Eq. (3) includes by definition the exchange rates with the environment for open systems. In the following section, we discuss how to take advantage of conservation laws to describe the exchange rates for $(U, V, N_1, \ldots, N_c)$ that appear on the right hand side of (3), particularly for the open flash-drum.

2.1. Conservation principles

In the reminder of the paper, we consider a flash-drum with one liquid phase on the bottom of a rigid vessel and a vapor phase on the top as the system of interest, see Fig. 2. The c chemical components inside the vessel are distributed between the two phases.

It is worth noting that throughout the paper we shall use indices l and g for the gas phase and for the liquid phase, respectively. In addition, we replace the phase-index by $\alpha \in \{l, g\}$ wherever it is convenient to have a more concise notation.

Each phase inside the flash-drum has certain amount of internal energy U_α (J), and a determined number of moles $N_{\alpha,j}$ (mol) for each component $j \in \{1, \ldots, c\}$. As the system is open, moles flow in and out at molar flow rates $F_{\alpha,N_j,\text{in}}$ (mol/s) and $F_{\alpha,N_j,\text{out}}$ (mol/s) respectively. Thermal energy is exchanged between each phase α and the environment at a rate Q_α (J/s) through a heat exchanger. Additionally, moles and energy can be exchanged between phases. We set the interface energy exchange rate as e (J/s) and the interface molar exchange rate as n (mol/s). These represent the rates at which total energy and total mole numbers are transported from/to the liquid to/from the gas phase. As a final consideration, we set K_α (J) to be the kinetic energy of the flow moving through phase α.

For modeling purposes, the following assumptions are considered:

- Each phase is perfectly mixed.
- Potential energy is constant over the whole process.
- Flow compressibility and viscous losses are negligible.
- Kinetic energy variations are negligible as compared to variations in enthalpy and/or in internal energy.
- No mole or energy accumulate in the interface.
- The liquid phase, the vapor phase, and the interface operate locally at thermodynamic equilibrium.[1]

It follows from Assumption A1 that the mole numbers dynamics for component $j \in \{1, \ldots, c\}$ corresponds to

$$\frac{dN_{g,j}}{dt}=F_{g,N_j,\text{in}}-\frac{N_{g,j}}{V_g}F_{g,V,\text{out}}+n_{g,j} \tag{4a}$$

$$\frac{dN_{l,j}}{dt}=F_{l,N_j,\text{in}}-\frac{N_{l,j}}{V_l}F_{l,V,\text{out}}-n_{l,j}. \tag{4b}$$

Under the assumptions considered in A2–A4, the internal energy can be written using a total energy balance

$$\frac{dU_g}{dt}=F_{g,H,\text{in}}-\frac{U_g}{V_g}F_{g,V,\text{out}}-P_gF_{g,V,\text{out}}-P_g\dot{V}_g+Q_g+e_g \tag{5a}$$

$$\frac{dU_l}{dt}=F_{l,H,\text{in}}-\frac{U_l}{V_l}F_{l,V,\text{out}}-P_lF_{l,V,\text{out}}-P_l\dot{V}_l+Q_l-e_l, \tag{5b}$$

and kinetic energy can be described using a balance on mechanical energy (derived from a momentum balance)

$$\frac{dK_g}{dt}=F_{g,K,\text{in}}-\frac{K_g}{V_g}F_{g,V,\text{out}}-P_g\dot{V}_g-P_gF_{g,V,\text{out}}+e_{g,K} \tag{6a}$$

$$\frac{dK_l}{dt}=F_{l,K,\text{in}}-\frac{K_l}{V_l}F_{l,V,\text{out}}-P_l\dot{V}_l-P_lF_{l,V,\text{out}}-e_{l,K}. \tag{6b}$$

In (4)–(6), $n_{\alpha,j}$ (mol/s), e_α (J/s) and $e_{\alpha,K}$ (J/s), $\alpha \in \{l, g\}$, represent interface sources/sinks for moles (in component j), total energy and mechanical energy, respectively. Volumetric outflow rates in (4)–(6) correspond to $F_{\alpha,V,\text{out}}$ (m^3/s), $\alpha \in \{l, g\}$. Inflow rates in (4)–(6), $F_{\alpha,N_j,\text{in}}$ (mol/s), $F_{\alpha,H,\text{in}}$ (J/s), $F_{\alpha,V,\text{in}}$ (m^3/s), and $F_{\alpha,K,\text{in}}$ (J/s), $\alpha \in \{l, g\}$, are assumed to be fixed. The time derivative of volume in (5) and (6) is represented as $\dot{V}_\alpha$ (m^3/s). As there is not a conservation principle for volume [19], we write the liquid volume as a function of the molar holdup [20]

$$V_l=\bar{v}_1N_{l,1}+\cdots+\bar{v}_cN_{l,c}, \tag{7a}$$

where $\bar{v}_j$ (m^3/s) corresponds to the partial molar volume of component j in the liquid phase. As the vessel containing both phases is rigid, the gas volume corresponds to the volume not occupied by the liquid phase

$$V_g=V_o-V_l, \tag{7b}$$

where V_o (m^3) represents the total fixed volume of the vessel. Volumetric outflow rates are described as a function of the phase flow velocity v_α (m/s), which in turn depends on the kinetic energy of the phase

$$F_{\alpha,V,\text{out}}=A_{\alpha,\text{out}}\ \ v_\alpha(K_\alpha,N_\alpha),\ v_\alpha=\sqrt{2K_\alpha/M_\alpha(N_\alpha)}, \tag{8}$$

where $A_{\alpha,\text{out}}$ (m^2) is the cross sectional area of the flow line, and $M_\alpha=\sum\bar{m}_jN_{\alpha,j}$ (kg) represents the mass holdup in bulk-phase α. Heat flows Q_α in the energy balance equation (5) are written as being proportional to differences between the heat exchanger temperature $T_{\alpha,Q}$ (K) and the bulk-phase temperature T_α (K)

$$Q_\alpha=\lambda_\alpha(T_{\alpha,Q}-T_\alpha), \tag{9}$$

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[1] Assumption A6 allows to locally apply (1) (together with other equilibrium relations) to the liquid phase, to the gas phase or to the interface even when a system is not at equilibrium. The reader interested in the particular conditions for the local equilibrium assumption is referred to the introduction in Kreuzer [18] and references therein.

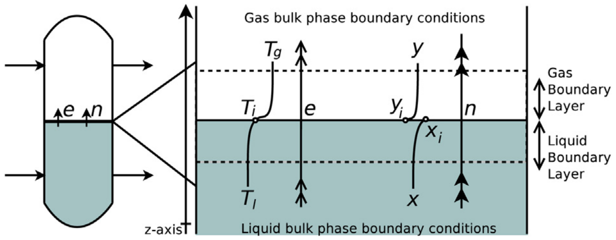

Fig. 3. Interface inside a non-equilibrium liquid–vapor system.

where λ_α (J/K·s) is a known heat exchange parameter. Temperature in turn is related to the internal energy. The internal energy for phase α can be written as

$$U_\alpha = U_{0,\alpha}(N_\alpha) + \mathcal{C}_\alpha(N_\alpha)(T_\alpha - T_0), \tag{10}$$

where $U_{0,\alpha}(\,\cdot\,) = \sum \bar{u}_{0,j} N_{\alpha,j}$ represents the internal energy of the system at a reference temperature T_0, and $\mathcal{C}_\alpha = \sum N_{\alpha,j}\,\bar{c}_{\alpha,j}$ (J/K) stands for the total heat capacity for phase α. The ideal gas equation is used to write the pressure in the gas phase as a function of the extensive variables

$$P_g(U_g, V_g, N_g) = \quad R\frac{N_g}{V_g}\left(T_0 + \frac{U_g - U_{0,g}(N_g)}{\mathcal{C}_g(N_g)}\right). \tag{11a}$$

An accurate description for the liquid pressure would require a detailed study on the hydrodynamic properties of the liquid subsystem, which is beyond the scope of this article. The interested reader is referred to the work of Teixeira and Secchi [21]. As the system is contained in a rigid vessel, from Pascal's principle, we assume that the interface, the liquid, and the gas phases are at the same (not necessarily constant) pressure

$$P_l = P_i = P_g(U_g, V_g, N_g). \tag{11b}$$

Eqs. (4)–(6) together with the constitutive equations (7)–(11) provide a standard dynamic representation of an open thermodynamic system. It should be noted here that the description is not yet completed as the interface exchange rates are not included in (7)–(11). To complete the flash-drum system description, we describe in the next section molar $n_{\alpha j}$, energetic e_α and mechanical $e_{\alpha,K}$ interface exchange rates as function of the intensive variables.

2.2. Interface exchange rates

The model presented so far considers the liquid and gas phases as separated subsystems inside the multiphase unit. As a consequence, the flash-drum is not required to evolve over an equilibrium manifold and inhomogeneities in temperature and chemical potential can arise between phases. The ideas behind the modeling for non-homogeneous systems were first presented by Krishnamurthy and Taylor [22]. Their model relies on describing interfacial temperature, pressure, and compositions solely based on the hypothesis supposed in A5 and A6 (plus a mechanical equilibrium assumption). The non-equilibrium model of Krishnamurthy and Taylor [22] is unfortunately limited to stationary regimes. Below, we extend such description adapted to our open process.

Two boundary layers are assumed to surround the gas–liquid interface as depicted in Fig. 3. Liquid and gas coexist in the interface between the layers at local equilibrium. Index i is set to describe local interfacial temperature and molar fractions. In addition, n is defined as the interface molar exchange which represents the total rate at which moles flow from liquid to gas phase. The interface variables are therefore referred as the vector

$$[T_i, \quad x_{1,i}, \quad y_{1,i}, \ldots, x_{c,i}, \quad y_{c,i}, n]^{t}. \tag{12}$$

Temperature and composition gradients are allowed between the bulk-phases and the interface, see Fig. 3. These gradients are known to be the driving forces behind interface flow rates. In the molar balance (4), the rate at which chemical component j flows from phase α towards/from the interface is represented by $n_{\alpha,j}$. Neglecting the effects of temperature, pressure gradients, and intercomponent diffusive transport, we can write [19]

$$n_{g,j} = k_{g,j}\,C_g(y_{j,i} - y_j) + n_g\,y_j \tag{13a}$$

$$n_{l,j} = k_{l,j}\,C_l(x_j - x_{j,i}) + n_l\,x_j, \tag{13b}$$

where y_j, x_j (mol/mol) and C_α (mol/m^3) represent respectively the molar fractions and concentrations in the bulk-phases. For phase $\alpha \in \{l, g\}$, the parameter $k_{\alpha j}$ (m^3/s) is assumed to be known and stands for a diffusive transport parameter. The total interface transport rates in (13) correspond simply to

$$n_\alpha = \sum_{j=1}^{c} n_{\alpha,j}.$$

The rates at which energy flows from phase α towards/from the interface in Eq. (5) are represented by e_α. The interface energy flow rates can be written as the sum of convective and thermal energy contributions [19,23]

$$e_g = \sum_{j=1}^{c} n_{g,j} \quad \bar{h}_{g,j} + \lambda_{g,i}(T_i - T_g) \tag{14a}$$

$$e_l = \sum_{j=1}^{c} n_{l,j} \quad \bar{h}_{l,j} + \lambda_{l,i}(T_l - T_i), \tag{14b}$$

where $\bar{h}_{\alpha,j}$ (J/mol) stand for the partial molar enthalpies of component j in phase α, $\lambda_{\alpha,i}$ (J/K·s) are known thermal exchange parameters, T_α (K) represent the bulk-phase temperature and T_i (K) is the interfacial temperature. The rates at which mechanical energy is exchanged between bulk-phase and the interface in the mechanical energy balance (6) are represented as $e_{\alpha,K}$. This terms correspond to [23]

$$e_{\alpha,K} = \frac{1}{2}v_{\alpha,i}^2 m_\alpha + \frac{P_\alpha}{\rho_\alpha} m_\alpha, \quad \alpha \in \{l, g\}, \tag{15}$$

where ρ_α (kg/m^3) stands for the density of the bulk-phase α. Setting $\bar{m}_j$ (kg/mol) to be the molar mass of component j, we write $m_\alpha = \sum \bar{m}_j\,n_{\alpha,j}$ for the mass interface transport rates. The term $v_{\alpha,i}$ (m/s) represents the average velocities of the mass flowing through the boundary layers surrounding the interface. Setting A_i (m^2) as the interface area we define the interface flow velocities in the boundary layer α as

$$v_{i,\alpha} = \frac{m_\alpha}{\rho_\alpha A_i}, \qquad \alpha \in \{l, g\}.$$

It should be noted that the interface exchange rates (13)-(15) depend on the $2c+2$ interface variables written in (12). These interface variables are recovered as the solution to an algebraic system of equations derived from the assumptions presented in A5 and A6.

2.3. Interface algebraic system

No accumulation of moles in the interface, Assumption A5, implies that $n_{l,j} + n_{g,j} = 0$. This allows to write $c-1$ equations

$$k_{g,j}\,C_g(y_{j,i} - y_j) - k_{l,j}\,C_l(x_j - x_{j,i}) + (y_j - x_j)n = 0, \quad j = 1, \ldots, c-1, \tag{16}$$

where $n := n_l = n_g$ is the total molar interface rate defined in (12). No accumulation of energy in the interface implies that $e_l + e_g = 0$, Assumption A5. This leads to one more algebraic restriction

$$\sum_{j=1}^{c} n_j \Delta\bar{h}_{\mathrm{vap},j} + \lambda_{g,i}(T_g - T_i) - \lambda_{l,i}(T_l - T_i) = 0, \tag{17}$$

where $n_j := n_{l,j} = n_{g,j}$ represents the molar interface rate for component j and $\Delta\bar{h}_{\mathrm{vap},j} = \bar{h}_{g,j} - \bar{h}_{l,j}$ represents the partial enthalpy of vaporization for component j. To complete the interface description we add $c+2$ interface equilibrium equations

$$0 = y_{j,i} - \psi_j(T_i, x_{1,i}, \ldots, x_{c,i})x_{j,i} \qquad j = 1, \ldots, c \tag{18a}$$

$$0 = 1 - \sum_{j=1}^{c} x_{j,i} \tag{18b}$$

$$0 = 1 - \sum_{j=1}^{c} y_{j,i}, \tag{18c}$$

where $\psi_j(\cdot)$ represents the liquid–vapor composition ratio for component j. Even though the liquid–vapor composition ratio is frequently assumed to be constant, this term is, in general, a nonlinear function of the intensive interface variables, see Eq. (B.6) in B.2.

Balance Eqs. (4)–(6) restricted by the interface Eqs. (16)–(18) sum to $4c+6$ nonlinear coupled differential algebraic equations that represent a semi-explicit DAE system

$$\frac{d\mathbf{z}}{dt} = f(\mathbf{z}, \mathbf{w}) \tag{19a}$$

$$0 = g(\mathbf{z}, \mathbf{w}), \tag{19b}$$

where $\mathbf{z}$ refers to bulk-phase variables

$$\mathbf{z} = [N_{g,1}\ldots N_{g,c} \quad N_{1,l}\ldots N_{l,c} \quad U_g \quad U_l \quad K_g \quad K_l]^{\mathrm{t}}, \tag{20a}$$

and $\mathbf{w}$ represents the interface variables.

$$\mathbf{w} = [y_{1,i}\ldots y_{c,i} \quad x_{1,i}\ldots x_{c,i} \quad T_i \quad n]^{\mathrm{t}}. \tag{20b}$$

The index of a DAE system is the number of times we have to differentiate the constraints $g(\cdot)$ to put aside the algebraic restrictions and write the DAE as an equivalent set of ordinary differential equations (ODEs). A DAE system has index one if and only if the Jacobian $J_{\mathbf{w}}(g)$ has full rank [24]. It follows from the implicit function theorem that, for an index-1 DAE description, there exists a unique function $h(\mathbf{z})$ such that substitution of $\mathbf{w} = h(\mathbf{z})$ satisfies the algebraic restriction in the DAE, *i.e.*, $g(\mathbf{z}, h(\mathbf{z})) = 0$. Therefore, if a DAE system is of index one, we can virtually solve the algebraic part through the mapping $\mathbf{w} = h(\mathbf{z})$. Substitution of $\mathbf{w} = h(\mathbf{z})$ into the differential part would transform a DAE model to an equivalent ODE system.

The Jacobian $J_{\mathbf{w}}(g)$ for Eq. (19b) is non singular (see A.1), therefore system (19) is of index one. The irreversible flash-drum DAE model is thus equivalent to an ODE system and it can be characterized using Lyapunov theory. In the next section we put together Gibbs Eq. (3) with balance Eq. (19a) to compute variations of entropy with respect to time. This forms the basis to calculate the entropy production, a positive definite thermodynamic potential, considered as a Lyapunov function candidate used to characterize the irreversible flash-drum.

3. Entropy production

In this section we compute the internal entropy production for the irreversible flash-drum using an entropy balance equation. Being positive definite, the internal entropy production represents a physics-based Lyapunov function candidate which we can use to characterize the dynamics for the nonlinear flash-drum system (19).

Entropy is an extensive non-conserved property [20]. The entropy production rate σ (J/K·s) for the open flash-drum can be written using an entropy balance as

$$\sigma = \sum_{\alpha \in \{g,l\}} \left(F_{\alpha,S,\mathrm{out}} - F_{\alpha,S,\mathrm{in}} - \frac{Q_\alpha}{T_{\alpha,Q}} \right) + \frac{dS}{dt}, \tag{21}$$

where $F_{\alpha,S,\mathrm{in}}$ (J/K·s) and $F_{\alpha,S,\mathrm{out}}$ (J/K·s) represent convective flow rates of entropy from/towards the environment, and Q_α (J/s) stands for an external heat source at temperature $T_{\alpha,Q}$ (K). Because entropy is additive over subsystems [12], entropy variations with respect to time can be written using Eq. (3) as

$$\frac{dS}{dt} = \sum_{\alpha \in \{g,l\}} \frac{dS_\alpha}{dt} = \sum_{\alpha \in \{g,l\}} \frac{1}{T_\alpha}\frac{dU_\alpha}{dt} + \frac{P_\alpha}{T_\alpha}\frac{dV_\alpha}{dt} + \frac{-\boldsymbol{\mu}_\alpha^{\mathrm{t}}}{T_\alpha}\frac{d\mathbf{N}_\alpha}{dt}, \tag{22}$$

where the vector notation

$$\boldsymbol{\mu}_\alpha = [\mu_{\alpha,1} \quad \ldots \quad \mu_{\alpha,c}]^{\mathrm{t}}, \mathbf{N}_\alpha = [N_{\alpha,1} \quad \ldots \quad N_{\alpha,c}]^{\mathrm{t}},$$

has been introduced. Note that $\dot{\mathbf{N}}_\alpha$ and $\dot{U}_\alpha$ in (22) represent the molar and energy balances for the flash-drum, equations (4)–(5), and $\dot{V}_\alpha$ can be recovered from the volume description (7).

Entropy for each phase is a homogeneous of degree one function, see Definition 1. Thus integration of dS_α gives [12,Euler's theorem]

$$S_\alpha = \frac{1}{T_\alpha}U_\alpha + \frac{P_\alpha}{T_\alpha}V_\alpha + \frac{\boldsymbol{\mu}_\alpha^{\mathrm{t}}}{T_\alpha}\mathbf{N}_\alpha, \quad \alpha \in \{g, l\}. \tag{23}$$

Each bulk-phase is perfectly mixed, as stated in A1. Then, multiplying (23) by the inverse of the residence time $1/\tau_\alpha = F_{\alpha,V,\mathrm{out}}/V_\alpha$ we can write the outflow rate of entropy as

$$F_{\alpha,S,\mathrm{out}} = \frac{1}{T_\alpha}F_{\alpha,U,\mathrm{out}} + \frac{P_\alpha}{T_\alpha}F_{\alpha,V,\mathrm{out}} + \frac{-\boldsymbol{\mu}_\alpha^{\mathrm{t}}}{T_\alpha}\mathbf{F}_{\alpha,N,\mathrm{out}}, \tag{24a}$$

where $F_{\alpha,Z,\mathrm{out}}$ holds for the convective flow rate of property Z, $F_{\alpha,Z,\mathrm{out}} = \tilde{Z}_\alpha F_{\alpha,V,\mathrm{out}}$, $Z \in \{S, U, \mathbf{N}\}$, and $\tilde{Z} = Z/V$ represents a variable per unit of volume. Rewriting Eq. (24a) using inflow instead of outflow properties we can write the convective entropy inflow rates as

$$F_{\alpha,S,\mathrm{in}} = \frac{1}{T_{\alpha,\mathrm{in}}}F_{\alpha,U,\mathrm{in}} + \frac{P_{\alpha,\mathrm{in}}}{T_{\alpha,\mathrm{in}}}F_{\alpha,V,\mathrm{in}} + \frac{-\boldsymbol{\mu}_{\alpha,\mathrm{in}}^{\mathrm{t}}}{T_{\alpha,\mathrm{in}}}\mathbf{F}_{\alpha,N,\mathrm{in}}. \tag{24b}$$

Substitution of (22) and (24) into (21) gives the entropy production expression for the irreversible flash-drum as

$$\begin{aligned} \sigma \quad = & \left(\frac{1}{T_g} - \frac{1}{T_{g,Q}}\right)Q_g + \left(\frac{1}{T_l} - \frac{1}{T_{l,Q}}\right)Q_l \\ & + \left(\frac{1}{T_g} - \frac{1}{T_{g,\mathrm{in}}}\right)F_{g,H,\mathrm{in}} + \left(\frac{1}{T_l} - \frac{1}{T_{l,\mathrm{in}}}\right)F_{l,H,\mathrm{in}} \\ & + \left(\frac{-\boldsymbol{\mu}_g^{\mathrm{t}}}{T_g} - \frac{-\boldsymbol{\mu}_{g,\mathrm{in}}^{\mathrm{t}}}{T_{g,\mathrm{in}}}\right)\mathbf{F}_{g,N,\mathrm{in}} + \left(\frac{-\boldsymbol{\mu}_l^{\mathrm{t}}}{T_l} - \frac{-\boldsymbol{\mu}_{l,\mathrm{in}}^{\mathrm{t}}}{T_{l,\mathrm{in}}}\right)\mathbf{F}_{l,N,\mathrm{in}} \\ & + \left(\frac{1}{T_g} - \frac{1}{T_l}\right)e + \left(\frac{-\boldsymbol{\mu}_g^{\mathrm{t}}}{T_g} - \frac{-\boldsymbol{\mu}_l^{\mathrm{t}}}{T_l}\right)\mathbf{n}. \end{aligned} \tag{25}$$

Each term in Eq. (25) can be identified as a source of entropy on a phenomenological basis:

- The first terms,

$$\left(\frac{1}{T_g} - \frac{1}{T_{g,Q}}\right)Q_g + \left(\frac{1}{T_l} - \frac{1}{T_{l,Q}}\right)Q_l,$$

represent the entropy produced as heat Q_α is exchanged between phase α and the external heat sources.

- The terms related with convective flow rates,

$$\sum_{\alpha\in\{g,l\}}\left(\frac{1}{T_\alpha}-\frac{1}{T_{\alpha,\mathrm{in}}}\right)F_{\alpha,H,\mathrm{in}}+\left(\frac{-\boldsymbol{\mu}_\alpha^t}{T_\alpha}-\frac{-\boldsymbol{\mu}_{\alpha,\mathrm{in}}^t}{T_{\alpha,\mathrm{in}}}\right)\mathbf{F}_{\alpha,N,\mathrm{in}},$$

represent the entropy produced as the inflows are mixed with the bulk-phases. Note that if inflows are at the same temperature and chemical potential (composition) as the bulk-phases, these terms are equal to zero.

- The last two terms,

$$\left(\frac{1}{T_g}-\frac{1}{T_l}\right)e+\left(\frac{-\boldsymbol{\mu}_g^{\mathrm{t}}}{T_g}-\frac{-\boldsymbol{\mu}_l^{\mathrm{t}}}{T_l}\right)\mathbf{n},$$

represent the entropy produced as energy and moles are exchanged through the interface when phases are not spatially homogeneous, *i.e.*, far from thermodynamic equilibrium.

Note that when the flash-drum is completely isolated from the environment we have $F_{\alpha,H,\mathrm{in}}=0$, $\mathbf{F}_{\alpha,N,\mathrm{in}}=0$ and $Q_\alpha=0$. Then, the entropy production is reduced to the internal entropy production

$$\sigma_i:=\sigma|_{\mathrm{isolated}}=\left(\frac{1}{T_g}-\frac{1}{T_l}\right)e+\left(\frac{-\boldsymbol{\mu}_g^{\mathrm{t}}}{T_g}-\frac{-\boldsymbol{\mu}_l^{\mathrm{t}}}{T_l}\right)\mathbf{n}. \tag{26}$$

Eq. (26) can be written as the sum of products between generalized flows and driving forces

$$\sigma_i:=\sigma|_{\mathrm{isolated}}=X_eJ_e+X_{n_1}J_{n_1}+\cdots+X_{n_c}J_{n_c},$$

where the flows, see Eqs. (13), (16) and (14),(17), correspond to

$$J_e:=\sum_{j=1}^{c}n_{g,j}\quad\bar{h}_{g,j}+\lambda_{g,i}(T_i-T_g)=\sum_{j=1}^{c}n_{l,j}\quad\bar{h}_{l,j}+\lambda_{l,i}(T_l-T_i) \tag{27a}$$

$$J_{n_j}:=k_{g,j}\,C_g(y_{j,i}-y_j)+n\,y_j=k_{l,j}\,C_l(x_j-x_{j,i})+n\,x_j, \tag{27b}$$

and the driving forces

$$X_e=\frac{1}{T_g}-\frac{1}{T_l},\quad X_{n_j}=\frac{-\mu_{g,j}}{T_g}-\frac{-\mu_{l,j}}{T_l} \tag{28}$$

come as a consequence of inhomogeneities between liquid and gas phases. Even though the flows (27) are not written using Onsager's relations [25], it can be easily verified that both (27) and (28) vanish at thermodynamic equilibrium. Moreover, numerical evidence shows that σ_i is positive definite and decreases with respect to time as the flash-drum reaches an equilibrium state in a system with fixed inflows, as shown in the next section.

4. Numerical simulations

In this section, a non-ideal methanol-water mixture is simulated to illustrate the properties of the model developed in Sections 2 and 3. First, a change of coordinates is used to transform the extensive–intensive description (19) to an equivalent DAE system improved for numerical integration. Then, a stability analysis based on Lyapunov first method is briefly discussed. Numerical trajectories demonstrate that the internal entropy production can be considered as a Lyapunov function candidate to assess the stability for the nonlinear irreversible flash-drum model.

4.1. Change of coordinates

Extensive variables in (19a) are considerably larger in magnitude than the intensive variables in the interface description (19b). Such differences are known to cause the Jacobian matrix of the system to be ill-conditioned [26]. This leads to precision problems during the numerical integration of a DAE or an ODE system. To avoid scale differences between the bulk-phase and the interface models, we use standard definitions for molar fractions and molar concentration together with constitutive equations (7)-(10) to write a change of coordinates

$$(N_{g,1}\ldots N_{g,c}\quad N_{l,j}\ldots N_{l,c}\quad U_g\quad U_l\quad K_g\quad K_l)\mapsto(y_1\ldots y_{c-1}\quad x_1\ldots x_{c-1}\quad T_g\quad T_l\quad F_{g,V,\mathrm{out}}\quad F_{l,V,\mathrm{out}}\quad C_g\quad V_l),$$

given by

$$y_j=N_{g,j}/N_g\quad j\in\{1,\ldots,c-1\} \tag{29a}$$

$$x_j=N_{l,j}/N_l\quad j\in\{1,\ldots,c-1\} \tag{29b}$$

$$T_\alpha=T_o+(U_\alpha-U_{\alpha,o})/\mathcal{C}_\alpha\qquad\alpha\in\{g,l\} \tag{29c}$$

$$F_{\alpha,V,\mathrm{out}}=A_{\alpha,\mathrm{out}}\sqrt{2K_\alpha/M_\alpha},\quad\alpha\in\{g,l\} \tag{29d}$$

$$C_g=N_g/(V_o-V_l) \tag{29e}$$

$$V_l=\bar{\mathrm{v}}N_l. \tag{29f}$$

Here, N_α and M_α represent the total molar and mass holdups for phase α, $U_{\alpha,o}$ is a reference state at temperature T_o, $\mathcal{C}_\alpha$ is the heat capacity for phase α, V_o is the volume of the flash-drum, and $\bar{\mathrm{v}}=\sum\bar{\mathrm{v}}_jx_j$ represents the liquid molar volume.

As the change of coordinates is bijective (A.2), time differentiation of (29) leads to a description of the flash-drum equivalent to (19) with the advantage that the bulk-phase and the interface variables have the same order of magnitude. Taking a time derivative on both sides of (29) allows to rewrite the DAE (19) as

$$\frac{d\boldsymbol{z}}{dt}=\mathrm{M}^{-1}\quad h(\boldsymbol{z},\mathbf{w}) \tag{30a}$$

$$0=g(\boldsymbol{z},\mathbf{w}), \tag{30b}$$

where

$$\boldsymbol{z}=[y_1\ldots y_{c-1}\quad x_1\ldots x_{c-1}\quad T_g\quad T_l\quad F_{l,V,\mathrm{out}}\quad F_{g,V,\mathrm{out}}\quad C_g\quad V_l]^{\mathrm{t}}$$

represents the new bulk-phase variables,

$$\mathbf{w}=[y_{1,i}\ldots y_{c,i}\quad x_{1,i}\ldots x_{c,i}\quad T_i\quad n]^{\mathrm{t}}$$

denotes again the interface variables, and M is a diagonal matrix of dimension $2c+4$

$$\mathrm{M}=\mathrm{diag}[C_gV_g1_{c-1}\quad C_lV_l1_{c-1}\quad\mathcal{C}_g\quad\mathcal{C}_l\quad\frac{M_g\nu_g}{A_{g,\mathrm{out}}}\quad\frac{M_l\nu_l}{A_{l,\mathrm{out}}}\quad V_g\quad 1], \tag{31}$$

where 1_{c-1} stands for a row vector of dimension $c-1$ with ones as elements. The entries in the vector function h in (30) are given by

$$\begin{aligned}
h_j &= F_{g,N,\text{in}}\left(y_{j,\text{in}}-y_j\right)+k_{g,j}C_g(y_{j,i}-y_j) && j\in\{1,\dots,c-1\}\\
h_{j+c-1} &= F_{l,N,\text{in}}\left(x_{j,\text{in}}-x_j\right)-k_{l,j}C_l(x_j-x_{j,i}) && j\in\{1,\dots,c-1\}\\
h_{2c-1} &= F_{g,N,\text{in}}\bar{\mathcal{C}}_{g,\text{in}}(T_{g,\text{in}}-T_g)+F_{g,V,\text{in}}P_{g,\text{in}}-F_{g,V,\text{out}}P_g\\
&\quad+\lambda_g(T_{g,Q}-T_g)+\lambda_{g,i}(T_i-T_g)-P_g\dot{V}_g+P_g n_{g,V}\\
h_{2c} &= F_{l,N,\text{in}}\bar{\mathcal{C}}_{l,\text{in}}(T_{l,\text{in}}-T_l)+F_{l,V,\text{in}}P_{l,\text{in}}-F_{l,V,\text{out}}P_l\\
&\quad+\lambda_l(T_{l,Q}-T_g)-\lambda_{l,i}(T_l-T_i)-P_l\dot{V}_l-P_l n_{l,V}\\
h_{2c+1} &= (0.5(v_{g,\text{in}}^2-v_g^2)\rho_{g,\text{in}}+P_{g,\text{in}})F_{g,V,\text{in}}\\
&\quad-P_g(F_{g,V,\text{out}}+\dot{V}_g)+(0.5(v_{i,g}^2-v_g^2)+P_g/\rho_g)m\\
h_{2c+2} &= (0.5(v_{l,\text{in}}^2-v_l^2)\rho_{l,\text{in}}+P_{l,\text{in}})F_{l,V,\text{in}}\\
&\quad-P_l(F_{l,V,\text{out}}+\dot{V}_l)-(0.5(v_{i,l}^2-v_l^2)+P_l/\rho_l)m\\
h_{2c+3} &= F_{g,V,\text{in}}C_{g,\text{in}}-F_{g,V,\text{out}}C_g+n-C_g\dot{V}_g\\
h_{2c+4} &= F_{l,V,\text{in}}C_{l,\text{in}}\bar{\text{v}}_{\text{in}}-F_{l,V,\text{out}}C_l\bar{\text{v}}-n_V,
\end{aligned}$$

where sub-index "in" refers to inflows, $\bar{\mathcal{C}}_{\alpha,\beta}$ (J/mol·K) represents molar heat capacity for the flow β in phase α, $m=\sum\bar{\text{m}}_j n_j$ holds for the interface mass exchange rate, $n_{l,V}=\sum\bar{\text{v}}_j n_j$ (m^3/s) represents the volumetric change rate at which the liquid phase evaporates, and $P_g n_{g,V}=nRT_g$ (J/s). The algebraic restriction g in (30), defined before in (19), is rewritten here for the sake of clarity

$$\begin{aligned}
g_j &= k_{g,j}\,C_g(y_{j,i}-y_j)-k_{l,j}\,C_l(x_j-x_{j,i})+(y_j-x_j)n\\
&\quad j\in\{1,\dots,c-1\}\\
g_c &= \sum_{j=1}^{c}n_j\Delta\bar{h}_{\text{vap}}+\lambda_{g,i}(T_g-T_i)-\lambda_{l,i}(T_l-T_i)\\
g_{j+c} &= y_{j,i}-\psi_j(T_i,x_{1,i},\dots,x_{c,i})x_{j,i} && j\in\{1,\dots,c\}\\
g_{2c+1} &= 1-\sum_{j=1}^{c}x_{j,i}\\
g_{2c+2} &= 1-\sum_{j=1}^{c}y_{j,i}.
\end{aligned}$$

Eq. (30) represents again an index one DAE system describing the irreversible flash-drum. The system has $2c+4$ bulk-phase variables and $2c+2$ interface variables. Conservation principles applied to each bulk-phase give $2c+4$ differential equations, while the interface is described by $2c+2$ algebraic equations. In contrast with (19), all the variables in (30) have the same order of magnitude, reducing the possibility of having numerical integration problems.

4.2. Local stability

In order to study the dynamic properties of the proposed model, we briefly review local stability results for linear index one DAE systems. A complete view on stability for DAE systems can be found in the work by Yang et al. [27].

Let $(\boldsymbol{z}^\star,\mathbf{w}^\star)$ be an equilibrium point of (19), *i.e.*:

$$\begin{aligned}
0 &= h(\boldsymbol{z}^\star,\mathbf{w}^\star)\\
0 &= g(\boldsymbol{z}^\star,\mathbf{w}^\star).
\end{aligned}$$

As the Jacobian $J_{\mathbf{w}}(g)$ is full ranked (see A.1), we can write a linearized version of (30) around as $(\boldsymbol{z}^\star,\mathbf{w}^\star)$ as

$$\frac{d\boldsymbol{z}}{dt}=\Theta\ \ (\boldsymbol{z}-\boldsymbol{z}^\star). \tag{32}$$

where the matrix Θ corresponds to the linearization of the right hand side terms in (30a) at the equilibrium point

$$\Theta=\left[J_{\boldsymbol{z}}(\text{M}^{-1}h)-J_{\mathbf{w}}(\text{M}^{-1}h)\ \ [J_{\mathbf{w}}(g)]^{-1}\ \ J_{\boldsymbol{z}}(g)\right]|_{(\boldsymbol{z}^\star,\mathbf{w}^\star)}. \tag{33}$$

Table 1
Numerical values for the stationary state.

$y_1^\star=0.6615$,	$y_2^\star=0.3385$	$T^\star=78.09^o\text{C}$,	$V_l^\star=0.1\ \ \text{m}^3$
$x_1^\star=0.2764$,	$x_2^\star=0.7236$	$C_g^\star=34.6874\text{mol}/\text{m}^3$,	$F_{\alpha,V}^\star=1\text{m}^3/\text{s}$

Lyapunov's first method states that if the spectrum of the matrix (33) is contained in the left half-complex plane, then (30) is locally asymptotically stable in a neighborhood of the stationary state $(\boldsymbol{z}^\star,\mathbf{w}^\star)$.

4.3. Case study

A non-ideal methanol-water mixture is considered to illustrate the proposed model and its analysis. With two components, the DAE system (30) is given by 14 equations and 14 variables. Fixing the inflows to be at thermodynamic equilibrium $(T^\star,P^\star,y_1^\star,y_2^\star,x_1^\star,x_2^\star)$, the stationary state for (30) corresponds to

$$\begin{aligned}
\boldsymbol{z}^\star &= (y_1^\star,x_1^\star,T^\star,T^\star,F_{g,V}^\star,F_{l,V}^\star,C_g^\star,V_l^\star)\\
\mathbf{w}^\star &= (y_1^\star,y_2^\star,x_1^\star,x_2^\star,T^\star,0),
\end{aligned}$$

where $C_g^\star$ is determined from Equation (11a), $V_l^\star$ is the volume of the liquid phase at equilibrium, and $F_{\alpha,V}^\star$ represents the stationary state volumetric inflow rates. To determine numerical values for the steady state, inflow properties are assumed to be at thermodynamic equilibrium[2] at $T^\star=351.24$ K (78.09 °C) and $P^\star=101.3$ kPa (0.9998 atm). In addition, inflows are fixed at 1 m^3/s, and the liquid phase is set to occupy 10% of the total volume $V_T=1$ m^3. At these conditions, the stationary state $(\boldsymbol{z}^\star,\mathbf{w}^\star)$ takes the values given in Table 1.

4.3.1. Stability analysis

Below we assess local stability when the system (30) is linearized through (32) at the stationary state given in Table 1.

- Scenario 1 (non-isobaric operation regime). At equilibrium, the linearized system (32) has rank 8. This system is unstable as the spectrum of the linearized model has two positive eigenvalues $\lambda_1\approx7.7691\times10^{-3}$, and $\lambda_2\approx1\times10^{-12}$. The remaining eigenvalues are contained in the left half plane, between $\lambda_3\approx-1$ and $\lambda_8\approx-1.2\times10^5$.
- Scenario 2 (isobaric operation regime). We calculate the stability properties of the system after a perfect pressure controller is included in (30) making pressure constant at $P_l=P_g=P^\star$. It must be noted here that the introduction of the perfect pressure controller changes the sytem's dynamics. Gas concentration trajectories are described under an isobaric regime by the algebraic restriction

  $$0=\frac{1}{R}\frac{dP_g}{dt}=C_g\frac{dT_g}{dt}+T_g\frac{dC_g}{dt}=\frac{T_g}{\mathcal{C}_g}h_{2c-1}+\frac{C_g}{V_g}h_{2c+3}, \tag{34}$$

  where functions h_{2c-1} and h_{2c+3} represent the right hand terms for the temperature and concentration derivatives in (30a):

  $$\begin{aligned}
  h_{2c-1} &:= F_{g,N,\text{in}}\bar{\mathcal{C}}_{g,\text{in}}(T_{g,\text{in}}-T_g)+F_{g,V,\text{in}}P_{g,\text{in}}-F_{g,V,\text{out}}P_g\\
  &\quad+\lambda_g(T_{g,Q}-T_g)+\lambda_{g,i}(T_i-T_g)-P_g\dot{V}_g+P_g n_{g,V}\\
  h_{2c+3} &:= F_{g,V,\text{in}}C_{g,\text{in}}-F_{g,V,\text{out}}C_g+n-C_g\dot{V}_g.
  \end{aligned}$$

---

[2] Liquid–vapor equilibrium is calculated using an Antoine–Margules thermodynamic model (see B.2)

Eq. (34) can be solved to write C_g as a state function. Then, the dimension of the linearized flash-drum is reduced as C_g is an equation of state for the isobaric system and not a state variable as in the non-isobaric model (30). Under the isobaric restriction (34) the linearized system (32) has rank 7.

One eigenvalue for (32) restricted by the isobaric equation (34) seems to be positive, $\lambda_1 \approx 1 \times 10^{-13}$. The rest of the spectrum is contained in the negative half-line between $\lambda_2 \approx -1$ and $\lambda_7 \approx -1.2 \times 10^5$. The positive eigenvalue is so close to zero that we cannot draw a sound conclusion about the stability as numerical error can be the underlying cause for the positivity of λ_1.

4.3.2. Numerical simulations for isobaric operation

Three dynamic simulations for Scenario 2 are now discussed that allows us to further investigate the stability of the isobaric regime. For the first scenario, the system is initialized at stationary state and the inflow liquid temperature is reduced, pushing the system far from the thermodynamic equilibrium state. In the second simulation, the system is disturbed from the stationary state. The disturbance is then removed at time $t = 2$s and the system goes back to the equilibrium state. For the last simulation we show how the internal entropy decreases as the system goes back to thermodynamic equilibrium starting from non-equilibrium initial states.

Numerical simulation 1 (Fig. 4). The inflow liquid temperature is disturbed through a ramp disturbance for $1 \leq t < 2$. The liquid inflow reaches a temperature $T_{l,\text{in}} = 0.95 \times T^{\star}$ for $t \geq 2$ and the liquid–vapor system is forced to operate far from thermodynamic equilibrium. As the system remains far from thermodynamic equilibrium, mass and energy flow between phases. As a consequence of the non-equilibrium operation, the liquid phase collapses around $t \approx 460$s. For better appreciation of the dynamic behavior in Numerical simulation 1, Fig. 4 is presented using a log scale for time.

Numerical simulation 2 (Fig. 5 and Fig. 6). A ramp disturbance is introduced in the liquid inflow temperature for $1 \leq t < 2$. In contrast with the numerical simulation 1, the disturbance is removed at $t = 2$s and the inflow temperature is set back its nominal value $T_{l,\text{in}} = T^{\star}$, see Fig. 5. This scenario is studied through two different disturbances. It can be seen in Fig. 6 that inhomogeneities in temperature and composition appear between phases as a consequence of the disturbance. Then, transfer processes redistribute the mass and the energy in the system as the flash-drum goes back to the equilibrium state.

Numerical simulation 3 (Fig. 7). Results from the Numerical simulation 2 point towards the equilibrium state being a stable steady state (Fig. 6), despite the presence of a zero eigenvalue in the linearized system (see Section 4.3.1). To extend the analysis, the last simulation presented here tests the internal entropy production (26) as a Lyapunov function candidate for the irreversible flash-drum[3] . In this scenario, the liquid–vapor system starts from an initial condition far from thermodynamic equilibrium while the inflows remain constant at the conditions in Table 1. It can be seen that the internal entropy production (26) behaves as a Lyapunov function as the irreversible flash-drum goes back to the stationary state, see Fig. 7. This suggests again that the thermodynamic equilibrium state is a stable stationary state for the irreversible flash-drum.

5. Conclusions and future work

In this paper, modeling aspects of dynamic flash-drum systems are explored using a non-equilibrium physics-based model. The description presented here considers transport phenomena as well as conservation principles to write the dynamics of a multiphase system as a nonlinear DAE system of index one. The proposed dynamic model describes the evolution of liquid and vapor phases as separated sub-systems interconnected through an interface. The introduction of the interface exchange rates in the model can even predict the collapse of one phase for systems that operate consistently far from equilibrium. Moreover, the model presented here describes how entropy is produced as a consequence of external (mass/energy exchanges between the system and the environment) and internal phenomena (mass/energy exchanges between phases).

Numerical evidence shows that the linearized irreversible flash-drum system has two positive eigenvalues for a non-isobaric operation regime. For the isobaric regime, one positive eigenvalue remains. This eigenvalue is so close to zero that it could be caused by the presence of numerical errors in the linearization process. Moreover, isobaric trajectories appear stable as the internal entropy production seems to be a Lyapunov function candidate for the system. The numerical results pinpoint the need to perform a deeper analysis regarding the stability for the nonlinear liquid–vapor irreversible system.

In future research, a nonlinear passivity-based stability analysis approach for the DAE model along the lines of García-Sandoval et al. [7] will be considered to get an input-output perspective on the analysis and control problem for multiphase chemical systems.

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Appendix A. Jacobians

A.1 Jacobian for the algebraic system g

The Jacobian of g, see Eq. (19), with respect to

$$\mathbf{w} = [y_{1,i} \ldots y_{c,i} \quad x_{1,i} \ldots x_{c,i} \quad T_i \quad n]^{\mathrm{t}}$$

corresponds to the full rank[4] $2c+2$ square matrix

$$J_{\mathbf{w}}(g) = \begin{bmatrix} C_g \mathrm{k}_g & C_l \mathrm{k}_l & 0_{(c-1,1)} & \mathbf{y}_{c-1} - \mathbf{x}_{c-1} \\ C_g \Delta \mathrm{h}_g \mathrm{k}_g & C_l \Delta \mathrm{h}_l \mathrm{k}_l & \lambda_{g,i} + \lambda_{l,i} & \mathbf{y}_c^{\mathrm{t}} \mathbf{h}_g - \mathbf{x}_c^{\mathrm{t}} \mathbf{h}_l \\ I_{(c,c)} & -\Psi - \mathrm{x}_i J_{\mathrm{x}_i}(\boldsymbol{\psi}) & -\mathrm{x}_i J_{T_i}(\boldsymbol{\psi}) & 0 \\ 0_{(1,c)} & 1_{(1,c)} & 0 & 0 \\ 1_{(1,c)} & 0_{(1,c)} & 0 & 0 \end{bmatrix}. \tag{A.1}$$

The term k_α in (A.1) represents a $(c-1) \times c$ diagonal sub-matrix with an additional column of zeros

$$\mathrm{k}_\alpha = \begin{bmatrix} k_{\alpha,1} & \cdots & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & k_{\alpha,c-1} & 0 \end{bmatrix}.$$

---

[3] Dynamic trajectories on the internal entropy production (26) are computed using the ideal gas model and the fugacity to calculate the chemical potentials (B.1).

[4] The Jacobian matrices and the respective ranks in A are calculated using the open source computer algebra system Maxima version:5.32.1.

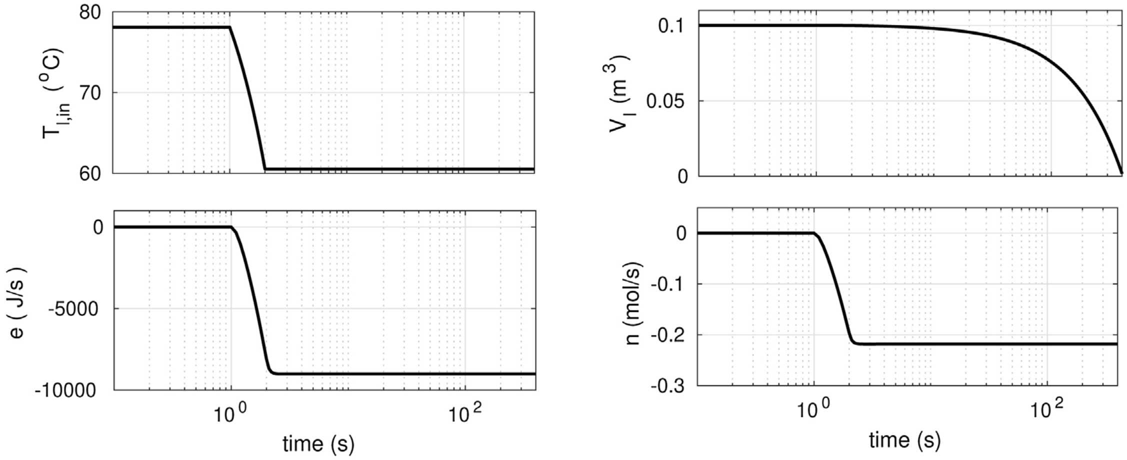

Fig. 4. Disturbance, liquid volume and interface flow rates for numerical simulation 1.

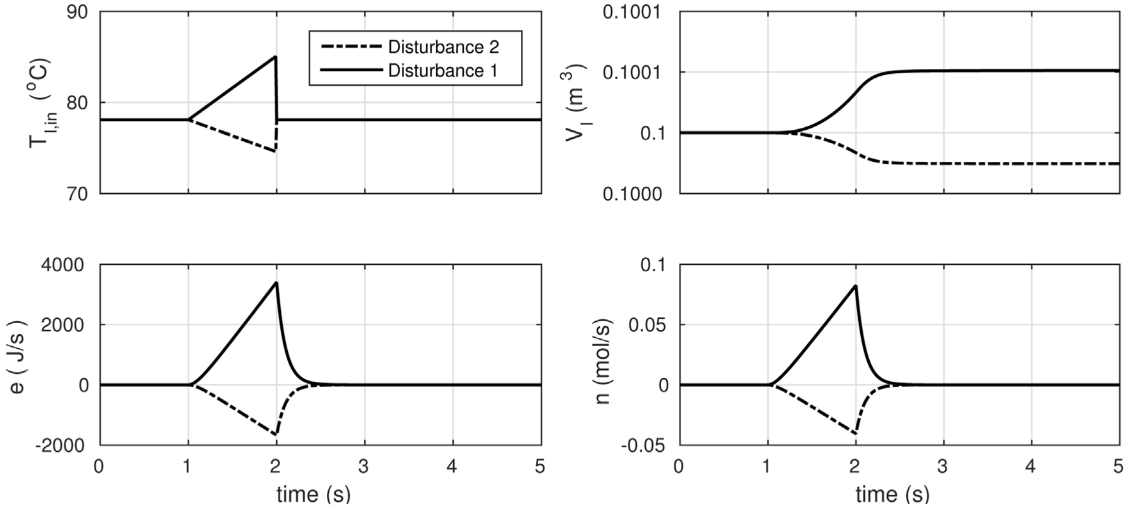

Fig. 5. Disturbance, liquid volume and interface flow rates for numerical simulation 2.

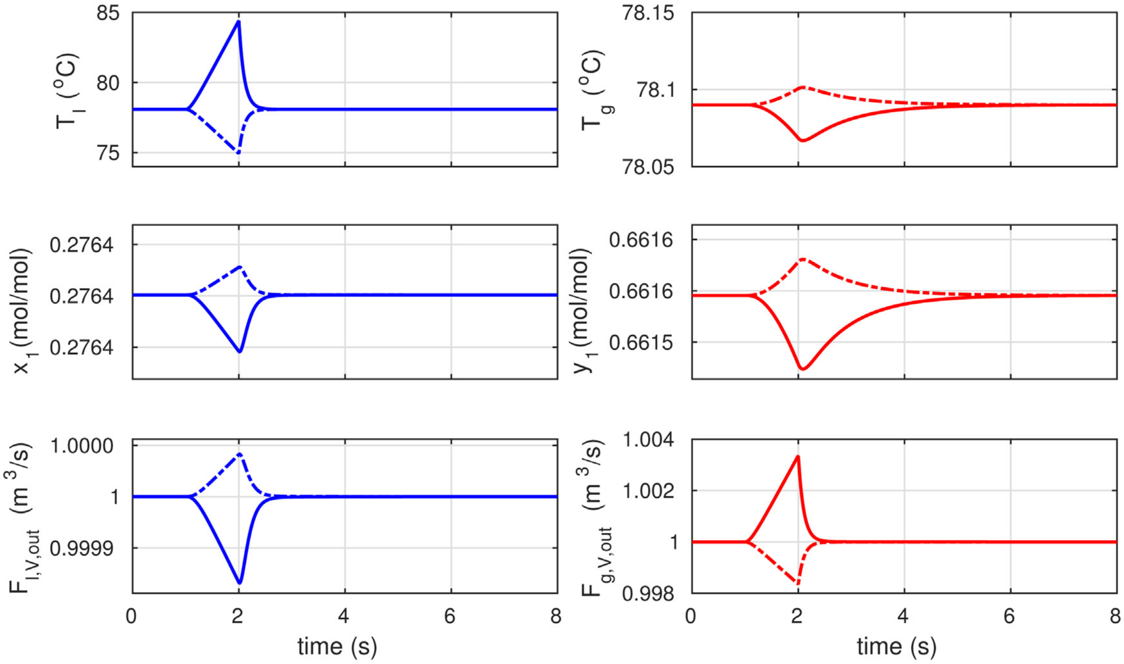

Fig. 6. Dynamic response for the methanol-water irreversible flash-drum against ramp disturbances: temperature, molar composition (methanol) and volumetric outflow trajectories against time; red plots (right) represent the gas phase, and blue plots (left) represent the liquid phase.

The terms y_c and x_c stand for a column vectors

$$\mathrm{y}_c = [y_1 \quad \dots \quad y_c]^{\mathrm{t}}, \mathrm{x}_c = [x_1 \quad \dots \quad x_c]^{\mathrm{t}}.$$

When subindex $c-1$ is used to write y_{c-1}, and x_{c-1}, the composition vector contains only the first $c-1$ molar fractions. The term $\Delta\mathrm{h}_\alpha$ represents a row vector

$$\Delta\mathrm{h}_\alpha = [\bar{h}_{\alpha,1} - \bar{h}_{\alpha,c} \quad \dots \quad \bar{h}_{\alpha,c-1} - \bar{h}_{\alpha,c}], \tag{A.2}$$

and the vector $\mathbf{h}_\alpha$ contains the enthalpies for the components in the mixture

$$\mathbf{h}_\alpha = [\bar{h}_{\alpha,1} \quad \dots \quad \bar{h}_{\alpha,c}]^{\mathrm{t}}. \tag{A.3}$$

The symbol x_i stands for a diagonal matrix with interface molar compositions

$$\mathrm{x}_i = \mathrm{diag}[x_{1,i} \quad \dots \quad x_{c,i}], \tag{A.4}$$

Ψ represents a diagonal matrix

$$\Psi = \mathrm{diag}[\psi_1, \dots, \psi_c]$$

and $J_\beta(K)$ holds for the Jacobians of the equilibrium ratio vector

$$\boldsymbol{\psi} = [\psi_1, \dots, \psi_c]^{\mathrm{t}}$$

with respect to $\beta \in \{x_{1,i} \dots x_{c,i} \; T_i\}$. Zeros and ones in (A.1) represent zero vectors, one vectors and scalars when dimension is not specified.

A.2 Jacobian for the change of coordinates

To show that that Equation (29) is bijective, it is enough to emphasize that the Jacobian matrix of the mapping is non-singular. To do so, we rewrite the change of coordinates as

$$\begin{aligned} F : (&N_{g,1}\dots N_{g,c} \quad N_{l,j}\dots N_{l,c} \quad U_g \quad U_l \quad K_g \quad K_l) \\ &\mapsto (y_1\dots y_{c-1} \quad x_1\dots x_{c-1} \quad T_g \quad T_l \quad F_{g,V,\mathrm{out}} \quad F_{l,V,\mathrm{out}} \quad C_g \\ &V_l), \end{aligned}$$

where

$$\begin{aligned} F_j &= N_{g,j}/N_g, & j &\in \{1, \dots, c-1\} \\ F_{j+c-1} &= N_{l,j}/N_l, & j &\in \{1, \dots, c-1\} \\ F_{2c-1} &= T_{\mathrm{o}} + (U_g - U_{g,o})/\mathcal{C}_g \\ F_{2c} &= T_{\mathrm{o}} + (U_l - U_{l,o})/\mathcal{C}_l \\ F_{2c+1} &= A_{g,\mathrm{out}}\sqrt{2K_g/M_g}, \\ F_{2c+2} &= A_{l,\mathrm{out}}\sqrt{2K_l/M_l}, \\ F_{2c+3} &= N_g/(V_o - V_l) \\ F_{2c+4} &= \bar{\mathrm{v}}N_l. \end{aligned}$$

Then the Jacobian of F with respect to

$$\mathbf{z} = [N_{g,1}\dots N_{g,c} \quad N_{l,j}\dots N_{l,c} \quad U_g \quad U_l \quad K_g \quad K_l]$$

corresponds to the full rank sparse matrix

$$\frac{\partial F}{\partial \mathbf{z}} = \begin{bmatrix} \frac{1}{N_g}\Theta_g(y) & 0_{(c-1,c)} & 0_{(c-1,1)} & 0_{(c-1,1)} & 0_{(c-1,1)} & 0_{(c-1,1)} \\ 0_{(c-1,c)} & \frac{1}{N_l}\Theta_l(x) & 0_{(c-1,1)} & 0_{(c-1,1)} & 0_{(c-1,1)} & 0_{(c-1,1)} \\ -\frac{1}{\mathcal{C}_g}\mathrm{u}_g & 0_{(1,c)} & \frac{1}{\mathcal{C}_g} & 0 & 0 & 0 \\ 0_{(1,c)} & -\frac{1}{\mathcal{C}_l}\mathrm{u}_l & 0 & \frac{1}{\mathcal{C}_l} & 0 & 0 \\ -\frac{F_{g,V,\mathrm{out}}}{M_g}\bar{\mathrm{m}} & 0_{(1,c)} & 0 & 0 & \frac{F_{g,V,\mathrm{out}}}{K_g} & 0 \\ 0_{(1,c)} & -\frac{F_{l,V,\mathrm{out}}}{M_l}\bar{\mathrm{m}} & 0 & 0 & 0 & \frac{F_{l,V,\mathrm{out}}}{K_l} \\ 0_{(1,c)} & \bar{\mathrm{v}} & 0 & 0 & 0 & 0 \\ -\frac{1}{V_g}\cdot 1_{(1,c)} & -C_g\bar{\mathrm{v}} & 0 & 0 & 0 & 0 \end{bmatrix}, \tag{A.5}$$

where $\Theta_g(\cdot)$ stands for a $(c-1) \times c$ matrix

$$\Theta_g = \begin{bmatrix} 1-y_1 & -y_1 & \cdots & -y_1 & -y_1 \\ -y_2 & 1-y_2 & \cdots & -y_2 & -y_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ -y_c & -y_c & \cdots & 1-y_c & -y_c \end{bmatrix}$$

and $\Theta_l(\cdot)$ holds for an equivalent matrix in terms of liquid molar fractions. The molar energy, the liquid molar volume, and the molar mass vectors in (A.5) correspond to

$$\bar{\mathrm{u}}_\alpha = [\bar{u}_{\alpha,1}, \dots, \bar{u}_{\alpha,c}], \qquad \bar{\mathrm{v}} = [\bar{\mathrm{v}}_1, \dots, \bar{\mathrm{v}}_c], \qquad \bar{\mathrm{m}} = [\bar{m}_1, \dots, \bar{m}_c].$$

Finally, the zeros and ones in (A.5) represent zero matrices/vectors, one vectors and scalars when dimension is not specified.

Table B.2
Dimensionless heat capacity $\mathrm{c_V}$ for ideal gases

	Gas	Temperature range
$\mathrm{c_V} = 3/2$	Monotonic non-interactive atoms	$T < 10^4\,\mathrm{K}$
$\mathrm{c_V} = 5/2$	Diatomic non-interactive molecules	$T < 10^3\,\mathrm{K}$
$\mathrm{c_V} = 7/2$	Diatomic non-interactive molecules	$T > 10^3\,\mathrm{K}$

Appendix B. Chemical potential and thermodynamic equilibrium

B.1 Chemical potential for gas and liquid mixtures

Consider a thermodynamic system formed by an ideal gas with internal energy U, and N moles occupying a volume V. The entropy for that system satisfies [12]

$$\mathrm{S} := N\bar{s} = N\bar{\mathrm{s}}_{\mathrm{o}} + N c_{\mathrm{V}} R \ln\left(\frac{U}{c_{\mathrm{V}}\,NR\,T_{\mathrm{o}}}\right) + NR\ln\left(\frac{V}{N\bar{\mathrm{v}}_{\mathrm{o}}}\right),$$

where the reference state $\bar{\mathrm{s}}_{\mathrm{o}}$ corresponds to the molar entropy for a system at temperature T_{o} with molar volume $\bar{\mathrm{v}}_{\mathrm{o}}$, and the dimensionless heat capacity $c_{\mathrm{V}} = c_v/R$ is considered a constant parameter. Values for $\mathrm{c_V}$ are reported in Table B.2.

For a mixture of ideal gases occupying a volume V at temperature T, entropy is the sum of entropies that each component would have if it alone were to occupy the volume V at temperature T [12,§3.4 – Gibbs theorem]. Then entropy for an ideal mixture of gases can be written as

$$\mathrm{S} = \sum_j N_j \bar{\mathrm{s}}_{\mathrm{o},j} + \mathcal{C}R\ln\left(\frac{U}{\mathcal{C}RT_{\mathrm{o}}}\right) + NR\ln\left(\frac{V}{N\bar{\mathrm{v}}_{\mathrm{o}}}\right) - R\sum_j N_j \ln y_j, \tag{B.1}$$

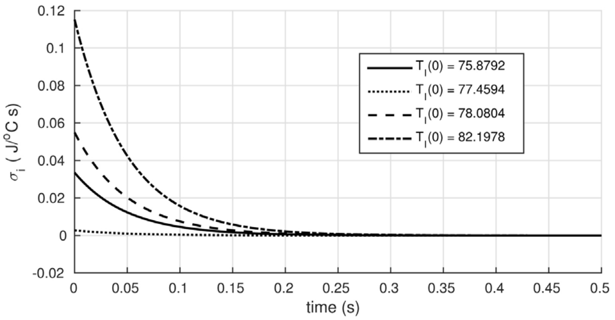

Fig. 7. Internal entropy production rate for the isobaric methanol-water irreversible flash-drum starting far from thermodynamic equilibrium (T_{eq} = 78. 09°C, P_{eq} = 101.3kPa).

where the sum is taken over all the components in the mixture, $N = \sum N_j$ stands for the total molar holdup of the system, and $\mathcal{C} = \sum c_{\text{v},j} N_j$ represents the total heat capacity of the system. Note that Equation (B.1) is the entropy fundamental equation defined by the thermodynamics formal structure (1) for an ideal gas mixture

$$S = S(U, V, N_1, \ldots, N_c).$$

It follows that chemical potential for component j inside an ideal gas mixture can be calculated as the derivative of (B.1) with respect to mole numbers

$$\frac{-\mu_j}{T} := \frac{\partial S}{\partial N_j} = \mu_j^\star(T, P) + RT \ln y_j \tag{B.2a}$$

where $\mu_j^\star(\cdot)$ represents the chemical potential of the ideal gas j,

$$\mu_j^\star = -Ts_{\text{o},j} + RT(c_{\text{v},j} + 1) - RT \ln \left(\frac{P_\text{o}}{P}\right)\left(\frac{T}{T_\text{o}}\right)^{c_{\text{v},j}+1}. \tag{B.2b}$$

Despite Equation (B.2a) being only valid for ideal gas mixtures, it is a common practice to try to preserve this form as far as possible when describing non-ideal systems [25].

The chemical potential for a component j inside a non-ideal mixture can be written as [25]

$$\mu_j = \mu_j^{\text{im}}(P, T) + RT \ln(\gamma_j),$$

where μ^{im} represents the chemical potential of component j inside an ideal mixture. To measure deviations from ideal behavior, excess in chemical potential (referred by some authors as excess on partial molar Gibbs potential $\bar{g}_i^{\text{ex}}$) is defined as

$$\mu_j^{\text{ex}} := \mu_j - \mu_j^{\text{im}},$$

and thus the activity coefficient γ_j is satisfies

$$\mu_j^{\text{ex}} = RT \ln \gamma_j.$$

Setting the chemical potential for j inside the ideal system μ_j^{im} to be represented by (B.2) we can write the chemical potential for component j inside a liquid mixture as

$$\mu_j = \mu_j^\star(T, P) + RT \ln x_j + \mu_j^{\text{ex}}. \tag{B.3}$$

This description for the chemical potential has a clear physical interpretation. The chemical potential μ_j is the chemical potential of j as an ideal system (an ideal gas in this case), plus mixing effects (second term), plus a correction term that represents deviations from ideal behavior μ^{ex}. In the following section, we write the excess in chemical potential μ_j^{ex} using a liquid–vapor equilibrium model.

B.2 Margules–Antoine equilibrium model

A liquid–vapor system with two components at temperature T and pressure P is said to be at thermodynamic equilibrium when the chemical potentials in liquid an gas phases are equal

$$\mu_{l,j} = \mu_{g,j}, \quad j \in \{1, 2\}. \tag{B.4}$$

As chemical potential is not measurable, it is common practice to rewrite (B.4) as an equivalent equality between fugacities

$$\bar{f}_j^g = x_j \gamma_j \bar{f}_j^l, \qquad j \in \{1, 2\}, \tag{B.5}$$

where $\bar{f}_j^g = y_j P$, provided that P is close to atmospheric pressure, stands for the gas fugacity for component j in the gas mixture, and

$$x_j \gamma_j \bar{f}_j^l = x_j \gamma_j \left(A_j - \frac{B_j}{T - C_j}\right) \exp\left(\frac{\mu_j^{\text{ex}}}{RT}\right).$$

Parameters A_j, B_j, and C_j, stand for constants for Antoine's Equation. The excess in chemical potential can be written as a function of a polynomial in the liquid composition $Q(x)$ [19]

$$\mu_j^{\text{ex}} = RT \left(-2Q + \frac{\partial Q}{\partial x_j}\right).$$

Given thermodynamic parameters A_{12} and A_{21}, the liquid composition polynomial Q can be written using Margules thermodynamic model as

$$Q = x_1 x_2 (A_{12} x_1 + A_{21} x_2).$$

Algebraic rearrangement of equation (B.5) leads to the nonlinear liquid–vapor equilibrium equation

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \psi_1 & 0 \\ 0 & \psi_2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}, \tag{B.6}$$

where

$$\psi_1 = \frac{1}{P}\left(A_1 - \frac{B_1}{T - C_1}\right) \exp\left(2A_{12}x_1x_2(1 - x_1) + A_{21}x_2^2(1 - 2x_1)\right)$$

$$\psi_2 = \frac{1}{P}\left(A_2 - \frac{B_2}{T - C_2}\right) \exp\left(2A_{21}x_1x_2(1 - x_2) + A_{12}x_1^2(1 - 2x_2)\right).$$

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