GEOMETRY OF THE FLASH DYNAMICS *

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Abstract

The qualitative behavior of the dynamics of an adiabatic flash with constant volumes and pressure is studied. If the phase equilibria are thermodynamically stable, the ordinary differential balance equations describing the dynamics can be interpreted as a gradient system on a Riemannian manifold where the metric derives from the Hessian matrices of the entropies and where the potential is the entropy production. When the feed remains constant, such a geometric interpretation insures asymptotic stability and proves the convergence without sustained oscillations to the steady-state where the entropy production is minimum.

1 Introduction

The dynamics of an adiabatic flash with constant volumes and pressure, analyzed in this paper, is a problem we addressed in the more general framework of the behavior of distillation processes. The main question deals with the asymptotic behavior, and so the stability, of such processes. One of the first major results is due to Rosenbrock (Rosenbrock, 1962) : he proved that the equations describing non ideal, binary, constant molar overflow continuous distillation columns with non theoretical plates (he introduced a so-called Murphree efficiency) and non negligible vapor holdup, has a unique globally asymptotically stable steady-state.

For multi-component multistage columns, most simulation studies (Gallun and Holland, 1982) indicate asymptotic stability. Nevertheless, some simulation studies relative to azeotropic distillation report the existence of multiple and possibly unstable steady-states (Magnussen et al, 1979; Prokopakis and Seider, 1983; Widalgo et al, 1989). It seems that Rosenbrock's result can not be extended to non binary distillation.

In this paper, we focus on the particular sub-problem of one stage distillation. We prove that, for an adiabatic flash with perfect holdup and pressure regulations, every steady-state

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is asymptotically stable without any restrictive assumption concerning the thermodynamics except that the phase equilibria are *thermodynamically stable*. This shows that, for one stage distillation, steady-state instability means hydraulic or thermodynamic instability. This characterization of the flash dynamics has been addressed firstly in Rouchon's thesis, 1990 and has been fully developed in Creff's thesis, 1992.

Our analysis relies on a geometric interpretation: the dynamics of an adiabatic flash with constant volumes and pressure and where the phase equilibria are thermodynamically stable, are described by a gradient system on a Riemannian manifold. The potential is then the entropy production (Glansdorff and Prigogine, 1971). Our derivation of the metric on the Riemannian manifold is in the spirit of the metric representation of equilibrium thermodynamics due to Weinhold (Weinhold, 1974) but is slightly different.

The paper content is as follows. We begin by some preliminaries relative to the formulation of phase equilibria relationships and thermodynamic stability conditions. Then we present the modeling differential-algebraic system and derive an equivalent ordinary differential system. Finally, the Riemannian structure and the gradient interpretation of the dynamics are described. In the conclusion, we sketch some open problems and explain why our analysis cannot be directly applied to multistage distillation columns.

2 Thermodynamic preliminaries

This section is devoted to an equivalent but rather unusual formulation of the thermodynamic equilibrium relationships that well suits our purpose.

We denote, for a mixture of c components, S the entropy, $N = (N_1, \dots, N_c)$ the mole quantities, H the enthalpy, v the volume, P the pressure, T the temperature and μ_i the chemical of component i. Since the pressure is considered as a parameter in the sequel, an adapted set of independent variables is H, N and P. Thus, S is considered as a function of H, N and P and satisfies the differential relation

$$TdS = dH - \sum_{i=1}^{c} \mu_i dN_i - vdP. \tag{1}$$

Consider now a closed system of c components which is maintained at a pressure P and which does not receive neither heat nor mass from the exterior. The second principle of the thermodynamics implies that the system tends towards an equilibrium state where the entropy is maximum under the constraints of constant enthalpy and mass holdups, respectively H and N. Denote p the number of possible phases. The thermodynamic equilibrium state is given by the solution of the optimization problem

$$\max_{\substack{H^1, N^1, \dots, H^p, N^p \\ \sum_{j=1}^{p} H^j = H, \ \sum_{j=1}^{p} N^j = N}} \left(\sum_{j=1}^{p} S^j(H^j, N^j, P) \right)$$

where the superscript j is relative to phase j. When the phase j is not present at the equilibrium, N^j and H^j are equal to 0. If all the p possible phases are present at the equilibrium, we have the equality of the first derivatives of the S^j:

$$\frac{\partial S^j}{\partial H^j} = \frac{\partial S^k}{\partial H^k} \quad \text{and} \quad \frac{\partial S^j}{\partial N^j} = \frac{\partial S^k}{\partial N^k} \tag{2}$$

for every j and k in $\{1, \dots, p\}$. These equilibrium conditions are equivalent to the classical ones (equality of temperatures and chemical potentials for all the phases).

The equilibrium equations (2) with the conservation constraints $H = \sum H^j$ and $N = \sum N^j$ do not insure that the entropy is maximum. They only mean that its first variation, δS, equals zero. If its second variation, $\delta^2 S$, is negative, the extremum is a (local) maximum. With the stability conditions on each phase j, such sufficient conditions on $\delta^2 S$, are called stability conditions. In order to avoid any confusion with other stability conditions, they will be called thermodynamic stability conditions. They are:

$$D^2 S^j \leq 0 \quad \text{and} \quad D^2 S^j + D^2 S^k < 0 \tag{3}$$

for all phases j and k ($j \neq k$) and where $D^2 S^j$ denotes the Hessian matrix of the entropy S^j with respect to the extensive variables (N^j, H^j). Notice that $D^2 S^j \leq 0$ results from the stability condition of phase j.

In the sequel, we consider only liquid-vapor equilibria. The liquid (resp. vapor) phase will be denoted with the superscript l (resp. v). We state the following assumption (thermodynamic stability):

TS: *the liquid-vapor equilibria are thermodynamically stable :*

$$D^2 S^l \leq 0, \quad D^2 S^v \leq 0 \quad \textit{and} \quad D^2 S^l + D^2 S^v < 0;$$

the ranks of $D^2 S^l$ and $D^2 S^v$ are equal to c.

Since the dependence of S^j with respect to H^j and N^j is homogeneous of degree one, we have the Euler identities (see the appendix), often called the Gibbs-Duhem relations :

$$\begin{aligned} S^j(H^j, N^j, P) &= DS^j(H^j, N^j, P) \cdot (H^j, N^j) \\ 0 &= D^2 S^j(H^j, N^j, P) \cdot (H^j, N^j) \end{aligned} \tag{4}$$

where DS^j and $D^2 S^j$ denote, respectively, the first and second derivatives of S^j with respect to the extensive variables (H^j, N^j) $(j = l, v)$ and where the dot "$\cdot$" corresponds to the evaluation of linear operators. Notice that the rank condition included in **TS** means that the concavity of S^j is strict excepted in the direction of (H^j, N^j).

For the azeotropic mixtures (the liquid and vapor have the same molar composition), assumption **TS** holds true in general since the dependence with respect to the enthalpies H^l and H^v of S^l and S^v are considered. For critical conditions (the liquid and the vapor become identical), $D^2 S^l + D^2 S^v$ is no more positive definite and **TS** is not satisfied.

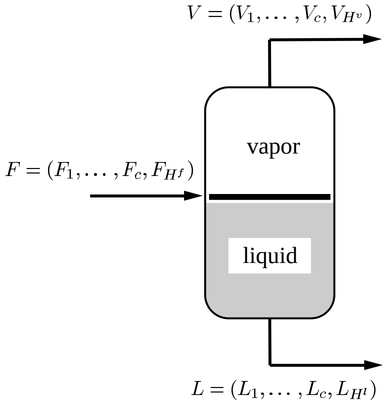

Figure 1: *an adiabatic flash drum where the pressure and the phase volumes are constant.*

3 Modeling

3.1 The modeling differential-algebraic system

Consider the adiabatic flash drum displayed on figure 1. Assume that :

- the pressure, liquid and vapor volumes are constant (perfect pressure and level regulators) ;
- the liquid and vapor phases are perfectly mixed and at thermodynamic equilibrium ;
- the thermodynamic equilibria satisfy **TS** at each time.

The dynamic behavior of this system is derived from the component and energy balance differential equations and from the equilibrium and holdup algebraic equations:

$$\left\{\begin{array}{rclcl} \dfrac{dR^l}{dt} + \dfrac{dR^v}{dt} & = & F - L - V & & \\ R^l & = & \dfrac{\upsilon^l(R^l)}{\upsilon^l(L)}\, L & = & \dfrac{\overline{\upsilon}^l}{\upsilon^l(L)}\, L \\ R^v & = & \dfrac{\upsilon^v(R^v)}{\upsilon^v(V)}\, V & = & \dfrac{\overline{\upsilon}^v}{\upsilon^v(V)}\, V \\ DS^l(R^l) & = & DS^v(R^v) & & \end{array}\right. \tag{5}$$

where

- $F = (F_1, \ldots, F_c, F_{H^f})$ corresponds to the component and enthalpy inflows (c is the number of components) ;
- $L = (L_1, \ldots, L_c, L_{H^l})$ (resp. $V = (V_1, \ldots, V_c, V_{H^v})$) corresponds to the liquid outflow (resp. vapor outflow) ;

- $R^l = (R_1^l, \ldots, R_c^l, R_{H^l})$ (resp. $R^v = (R_1^v, \ldots, R_c^v, R_{H^v})$) corresponds to the component and enthalpy holdups of the liquid phase (resp. vapor phase) ;
- S^l (resp. S^v) is the liquid (resp. vapor) entropy function. DS^l (resp. DS^v) denotes the first derivative of S^l (resp. S^v) with respect to R^l (resp. R^v);
- v^l (resp. v^v) is the liquid (resp. vapor) volume function (see previous section, equation (1)); $v^l(L)$ (resp. $v^v(V)$) corresponds to the liquid (resp. vapor) volume flow;
- $\overline{v}^l$ (resp. $\overline{v}^v$) is the liquid (resp. vapor) volume which is assumed constant.

The second (resp. third) equation of (5) insures simultaneously that

- the liquid (resp. vapor) holdup has the same composition than the liquid (resp. vapor) flow leaving the flash drum ;
- the liquid (resp. vapor) holdup is constant.

In (5), we have not recalled the dependence with respect to the pressure for S^l, S^v, v^l and v^v since it is assumed constant. Notice that the number of unknown variables (R^l, R^v, L et V), $4(c+1)$, is equal to the number of equations. Notice also that, because of homogeneity, we can consider independently $v^l(R^l)$ and $v^l(L)$, $v^v(R^v)$ and $v^v(V)$.

3.2 Transformation into an ordinary differential system

For sake of clarity, the dependence of the differentials with respect to R^l and R^v is recalled only when necessary. Denote $\tau^l(L) = \dfrac{\overline{v}^l}{v^l(L)}$ and $\tau^v(V) = \dfrac{\overline{v}^v}{v^v(V)}$ the resident times in the liquid and the vapor. We have $R^l = \tau^l(L)\, L$, $R^v = \tau^v(V)\, V$.

The first difficulty comes from the implicit character of (5). Such a system is called an differential algebraic system. One can give a measure of its implicit character through the notion of index, which here equals 2 (Sincovec et al, 1981 –for linear systems–; Fliess, Lvine and Rouchon 1992 –for general implicit systems–).

The modeling system (5) can be rewritten explicitly as indicated by the following lemma.

Lemma 1. *The solutions of (5) coincide with the solutions of the ordinary differential system*

$$\left\{ \begin{array}{rcl} \dfrac{dR^l}{dt} & = & \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot \left(F - \dfrac{R^l}{\tau^l} - \dfrac{R^v}{\tau^v}\right) \\ \dfrac{dR^v}{dt} & = & \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \cdot \left(F - \dfrac{R^l}{\tau^l} - \dfrac{R^v}{\tau^v}\right) \end{array} \right. \tag{6}$$

with

$$\left\{ \begin{array}{rcl} \dfrac{1}{\tau^l} & = & \dfrac{Dv^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot F}{\overline{v}^l} \\ \dfrac{1}{\tau^v} & = & \dfrac{Dv^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \cdot F}{\overline{v}^v}. \end{array} \right. \tag{7}$$

and initial conditions (R^l_0, R^v_0) *satisfying*

$$DS^l(R^l_0) = DS^v(R^v_0), \quad v^l(R^l_0) = \overline{v}^l \quad \textit{and} \quad v^v(R^v_0) = \overline{v}^v.$$

Proof According to 5, we have

$$D^2S^l(R^l) \cdot \frac{dR^l}{dt} = D^2S^v(R^v) \cdot \frac{dR^v}{dt}.$$

Assumption **TS** implies that $D^2S^l + D^2S^v$ is regular. Thus

$$\begin{cases} \dfrac{dR^l}{dt} &= \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot \dfrac{dR}{dt} \\ \dfrac{dR^v}{dt} &= \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \cdot \dfrac{dR}{dt} \end{cases}$$

where $R = R^l + R^v$ and $\dfrac{dR}{dt} = F - L - V = F - \dfrac{R^l}{\tau^l} - \dfrac{R^v}{\tau^v}$.

It remains to express τ^l and τ^v as functions of R^l, R^v, $\overline{v}^l$, $\overline{v}^v$ and F. Let us detail the computation of τ^l. Since the liquid and vapor volumes are constant, we have

$$Dv^l \cdot \frac{dR^l}{dt} = 0,$$

that is

$$Dv^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot (F - \frac{R^l}{\tau^l} - \frac{R^v}{\tau^v}) = 0.$$

The Gibbs-Duhem relations imply $D^2S^v \cdot R^v = 0$, so

$$\frac{1}{\tau^l} = \frac{Dv^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot F}{Dv^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot R^l}$$

Similarly, $\left[D^2S^l + D^2S^v\right] \cdot R^l = D^2S^v \cdot R^l$, that is

$$\left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot R^l = R^l$$

As

$$Dv^l \cdot R^l = v^l(R^l) = \overline{v}^l,$$

we obtain (7) for $\dfrac{1}{\tau^l}$.

To conclude, we verify that $DS^l(R^l) - DS^v(R^v)$, $v^l(R^l)$ and $v^v(R^v)$ are first integrals of (6), so that :

- if the liquid and vapor phases are initially at thermodynamic equilibrium, then, for all subsequent times, they are at thermodynamic equilibrium: $DS^l(R^l_0) = DS^v(R^v_0)$ implies $DS^l(R^l_t) = DS^v(R^v_t)$ for all $t \geq 0$;
- the liquid and vapor volumes remain constant along every trajectory : $v^l(R^l_t) = v^l(R^l_0)$ and $v^v(R^v_t) = v^v(R^v_0)$ for all $t \geq 0$. ■

4 The gradient system

As displayed on figure 2, we will prove that the dynamical system described by (5) is a gradient system on a Riemannian manifold (see the appendix)

4.1 The Riemannian structure

The following construction is in the spirit of the metric formulation of the equilibrium thermodynamics that has been proposed by Weinhold (Weinhold, 1974) . However, for our purpose, we do not consider directly the Gibbs space of the entropy, mole quantities and volume. The basic space, where our equilibrium manifold is embedded, is the Cartesian product $]0,+\infty[^{c+1} \times]0,+\infty[^{c+1}$ of the liquid holdup space with the vapor holdup space.

Consider the sub-manifold Σ of $]0,+\infty[^{c+1} \times]0,+\infty[^{c+1}$ defined by the following equations:

$$\begin{array}{rcl}\Sigma & = & \big\{ M = (R^l, R^v) \in]0,\infty[^{c+1} \times]0,\infty[^{c+1}, \text{ such that:} \\ & & \qquad DS^l(R^l) = DS^v(R^v),\ v^l(R^l) = \overline{v}^l \text{ and } v^v(R^v) = \overline{v}^v . \big\}\end{array} .$$

Notice that the equations defining Σ are independent, that is to say that the $(c+3) \times 2(c+1)$ Jacobian matrix

$$\begin{pmatrix} D^2 S^l & -D^2 S^v \\ Dv^l & 0 \\ 0 & Dv^v \end{pmatrix}$$

has full rank $c+3$. This results directly from the Gibbs-Duhem relations (4) and assumption **TS**.

The tangent space at $M \in \Sigma$, $T\Sigma_M$, can be identified to the sub-space of the vectors $(\alpha^l, \alpha^v) \in \mathbb{R}^{c+1} \times \mathbb{R}^{c+1}$ such that

$$D^2 S^l \cdot \alpha^l = D^2 S^v \cdot \alpha^v,\ Dv^l \cdot \alpha^l = 0 \text{ and } Dv^v \cdot \alpha^v = 0,$$

where the operators D^2S^l, D^2S^v, Dv^l and Dv^v are evaluated at M.

For each $M \in \Sigma$, we consider the quadratic form

$$\begin{array}{rccl} Q_M : & T\Sigma_M & \longrightarrow & \mathbb{R} \\ & (\alpha^l, \alpha^v) & \longrightarrow & Q_M(\alpha^l, \alpha^v) = -{}^t\alpha^l \cdot D^2 S^l \cdot \alpha^l -{}^t \alpha^v \cdot D^2 S^v \cdot \alpha^v \end{array} \tag{8}$$

where ^{t} denotes transposition and where D^2S^l and D^2S^v are the Hessian matrices of S^l and S^v evaluated at point $M = (R^l, R^v)$.

Lemma 2. *For each $M \in \Sigma$, Q_M defines an Euclidian structure on $T\Sigma_M$. Otherwise stated, (Σ, Q) is a Riemannian manifold.*

Proof Clearly, Q_M is non-negative (assumption **TS**). It remains to be proved that Q_M is non-degenerate. Consider $(\alpha^l, \alpha^v) \in T\Sigma_M$ such that $Q_M(\alpha^l, \alpha^v) = 0$. Then, ${}^t\alpha^l \cdot D^2S^l \cdot \alpha^l = 0$ and ${}^t\alpha^v \cdot D^2S^v \cdot \alpha^v = 0$. Assumption **TS** implies that α^l is proportional to R^l and α^v to R^v. But $Dv^l \cdot \alpha^l = 0$ and $Dv^l \cdot R^l = \overline{v}^l > 0$. Thus $\alpha^l = 0$. Similarly, $\alpha^v = 0$. ■

4.2 The dynamics derive from a potential

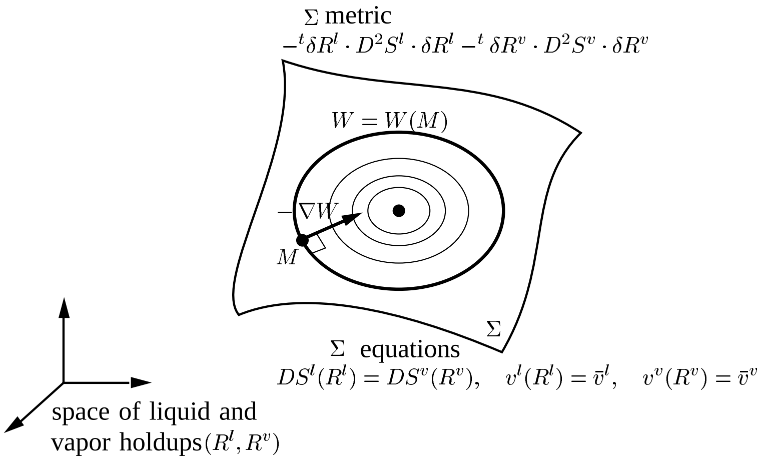

Figure 2: *the dynamic behavior of an adiabatic flash is described by a gradient system on the equilibrium Riemannian manifold* Σ *the potential of which is the entropy production* W.

4.2.1 The entropy production

The entropy holdup S is given by

$$S = S^l(R^l) + S^v(R^v).$$

The results that Prigogine and Glansdorff (Glansdorff and Prigogine, 1971; Prigogine, 1961) have obtained for dissipative systems can be directly applied here: the entropy production

$$W = \frac{dS}{dt} - (\mathcal{S}^f - \mathcal{S}^l - \mathcal{S}^v),$$

is non negative ($\mathcal{S}^f$ is the entropy flow of the feed, $\mathcal{S}^l = S^l(L)$ (resp. $\mathcal{S}^v = S^v(V)$) is the liquid (resp. vapor) entropy outflow). As shown in Rouchon's thesis (Rouchon 1990) , this can be directly proved from the modeling system (5). We have

$$\frac{dS}{dt} = DS^l \cdot \frac{dR^l}{dt} + DS^v \cdot \frac{dR^v}{dt}.$$

Since $DS^l = DS^v$ and $\dfrac{d(R^l + R^v)}{dt} = F - L - V$, we obtain

$$\frac{dS}{dt} = DS^l \cdot F - DS^l \cdot L - DS^v \cdot V.$$

But, by homogeneity, $\mathcal{S}^l = DS^l \cdot L$ and $\mathcal{S}^v = DS^v \cdot V$. Thus

$$W = DS^l \cdot F - \mathcal{S}^f. \tag{9}$$

Consider now the flows F^l and F^v associated to the liquid and vapor flows corresponding to a steady-state. They are solutions of the optimization problem:

$$\max_{\substack{F^l,\ F^v \\ F^l + F^v = F}} \left(S^l(F^l) + S^v(F^v) \right).$$

Replacing F by $F^l + F^v$ and using the homogeneity of S^l and S^v, we obtain

$$W = \left(DS^l(L) - DS^l(F^l) \right) \cdot F^l + \left(DS^v(V) - DS^v(F^v) \right) \cdot F^v + S^l(F^l) + S^v(F^v) - \mathcal{S}^f.$$

To go further, we need the following result: if ϕ is a real concave and homogeneous function of degree 1 depending on $x \in]0, \infty[^n$ such that the rank of $\dfrac{\partial^2 \phi}{\partial x^2}$ equals $n - 1$, then, for all $a \in]0, +\infty[$, we have $\displaystyle\min_{x \in]0,+\infty[^n} \left(\left[\frac{\partial \phi}{\partial x} \right]_a x - \phi(x) \right) = 0.$

Assumption **TS** and the previous result give

$$\left(DS^l(L) - DS^l(F^l) \right) \cdot F^l \geq 0 \quad \text{and} \quad \left(DS^v(V) - DS^v(F^v) \right) \cdot F^v \geq 0.$$

The definitions of F^l and F^v imply

$$S^l(F^l) + S^v(F^v) - \mathcal{S}^f \geq 0.$$

This proves that the entropy production W, given by (9), is always non-negative. Moreover, it is minimum at the equilibrium.

At the exception of the constant term $S^l(F^l) + S^v(F^v) - \mathcal{S}^f$, the entropy production is in the standard form

$$W = \sum_\alpha J_\alpha X_\alpha,$$

introduced by Prigogine and Glansdorff and where the terms J_α are the flows associated to the generalized thermodynamic forces X_α. Here, the flow terms are F^l and F^v and the generalized thermodynamic forces are $DS^l(L) - DS^l(F^l)$ and $DS^v(V) - DS^v(F^V)$.

The universal evolution criterion of Glansdorff and Prigogine says that the evolution of every macroscopic dissipative system whose entropy production is given by $\sum_\alpha J_\alpha X_\alpha$ satisfies the fundamental inequality

$$\sum_\alpha J_\alpha \frac{dX_\alpha}{dt} \leq 0.$$

For our macroscopic system, one directly derives the stability when the feed F remains constant: since the flow terms F^l and F^v are constant, $\dfrac{dW}{dt} \leq 0$. Moreover, it is easily proved that $\dfrac{dW}{dt} = 0$ if and only if $\dfrac{dR}{dt} = 0$. Otherwise stated, W is a Lyapunov function (see for example Arnold, 1974) and the asymptotic stability is insured. This stability analysis can be enriched by showing that the dynamics derive from a potential, which is a stronger property than the existence of a Lyapunov function.

4.2.2 The gradient system

Theorem 1. *The dynamical system described by (5) derives from the potential (the entropy production)*

$$W = DS^l \cdot F - \mathcal{S}^f$$

on the Riemannian manifold (Σ, Q)*:*

$$\frac{dM}{dt} = -\nabla W$$

where ∇ *denotes the gradient operator associated to the metric* Q *and* $M = (R^l, R^v)$ *is the current point on* Σ*.*

This result implies that :

- if the feed F remains constant, the potential W satisfies

  $$\frac{dW}{dt} = -Q_M(\nabla W) \leq 0.$$

  It is (locally) minimal at every steady-state. Thus, every steady-state is locally asymptotically stable.

- around every steady-state, all the eigenvalues are real and negative: in local coordinates on Σ, the jacobian matrix of the system equals $-AB$, where A and B are matrices representing positive definite quadratic forms (A is the inverse of the metric matrix and B is the Hessian matrix of the potential W). This jacobian matrix is diagonalizable with real negative eigenvalues; this derives from a classic result on regular matrices pencils (Gantmacher, 1966).

Proof We have to prove that the coordinates of the gradient of W in the vector space $\mathbb{R}^{c+1} \times \mathbb{R}^{c+1}$ are given by the right-hand side of (6). Otherwise stated, according to the definition of the gradient, if we find $(g^l, g^v) \in T\Sigma_M$ satisfying, for all $(\alpha^l, \alpha^v) \in T\Sigma_M$,

$$\begin{aligned} -{}^t\alpha^l \cdot D^2S^l \cdot g^l -{}^t \alpha^v \cdot D^2S^v \cdot g^v &= -DW \cdot (\alpha^l, \alpha^v) \\ &= -{}^t\alpha^t \cdot D^2S^l \cdot F = -{}^t\alpha^v \cdot D^2S^v \cdot F, \end{aligned} \tag{10}$$

then necessarily (g^l, g^v) are the components of ∇W in the vector space $\mathbb{R}^{c+1} \times \mathbb{R}^{c+1}$ containing $T\Sigma_M$.

According to 1, we state

$$\begin{aligned} g^l &= \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot \left(F - \frac{R^l}{\tau^l} - \frac{R^v}{\tau^v}\right) \\ g^v &= \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \cdot \left(F - \frac{R^l}{\tau^l} - \frac{R^v}{\tau^v}\right) \end{aligned}$$

and show that g^l et g^v belong to $T\Sigma_M$. We have

$$D^2S^l \cdot g^l = D^2S^v \cdot g^v.$$

This results from

$$\begin{aligned}
D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v &= D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \\
&\quad +D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&\quad -D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&= D^2S^l - D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&= D^2S^l - D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&\quad +D^2S^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&\quad -D^2S^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \\
&= D^2S^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l,
\end{aligned}$$

that is

$$D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v = D^2S^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l.$$

Relations (7) together with the Gibbs-Duhem relations $D^2S^l \cdot R^l = 0$ and $D^2S^v \cdot R^v = 0$ imply that

$$Dv^l \cdot g^l = 0 \text{ and } Dv^v \cdot g^v = 0.$$

Consequently, $(g^l, g^v) \in T\Sigma_M$.

Now we take $(\alpha^l, \alpha^v) \in T\Sigma_M$. Remembering $D^2S^l \cdot \alpha^l = D^2S^v \cdot \alpha^v$, we have

$$\begin{aligned}
-{}^t\alpha^l \cdot D^2S^l \cdot g^l -{}^t \alpha^v \cdot D^2S^v \cdot g^v &= -{}^t\alpha^l \cdot D^2S^l \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^v \cdot F \\
&\quad -{}^t\alpha^v \cdot D^2S^v \cdot \left[D^2S^l + D^2S^v\right]^{-1} \cdot D^2S^l \cdot F \\
&= -{}^t\alpha^l \cdot D^2S^l \cdot F \\
&= -{}^t\alpha^v \cdot D^2S^v \cdot F \\
&= -DW \cdot (\alpha^l, \alpha^v)
\end{aligned}$$

The (g^l, g^v), satisfying (10) for every tangent vector (α^l, α^v), are the components of ∇W in $\mathbb{R}^{c+1} \times \mathbb{R}^{c+1}$. ■

5 Conclusion

The above analysis can be done for an isothermal flash drum. The entropy function S must be replaced by the Gibbs energy function G. Similarly, the introduction of more than two phase does not require any substantial modification. The problem is far more complex when additional stages are considered: this is due to the fact that, contrarily to the single stage case, the entropy production is not minimum at the steady-state and, consequently, cannot be a Lyapunov function. As related in the introduction, several numerical studies seem to indicate the existence of unstable steady-states for multistage distillation. In the light of the present study, it appears interesting to complete such simulations by investigating separately the thermodynamic and hydraulic stability. This would be the beginning of an answer to the following question: does there exist, for continuous distillation columns, unstable steady-states when the hydraulic effects are fast and asymptotically stable (constant pressures and volumes) and when, on each stage, the phase equilibria are thermodynamically stable?

Notations

$j = \{l, v\}$	liquid and vapor phases superscripts
c	number of components in the mixture
$F = (F_1, \dots, F_c, F_{H^f})$	flash component and enthalpy inflows (mol/s and J/s)
(g^l, g^v)	components of the gradient of the potential W (mol/s and J/s)
H^j	enthalpy function of phase j (J)
$L = (L_1, \dots, L_c, L_{H^l})$	flash component and enthalpy liquid outflow (mol/s and J/s)
$N^j = (N^j_1, \dots, N^j_c)$	number of mole quantities of phase j (mol)
P	equilibrium pressure (Pa)
Q_M	metric on $T\Sigma_M$ (J/K/mol^2 and1/K/J)
$R^j = (R^j_1, \dots, R^j_c, R_{H^j})$	flash component and enthalpy holdup for phase j (mol and J)
S^j	entropy of phase j (J/K)
$\mathcal{S}^f$	entropy flow of the feed (J/K/s)
$\mathcal{S}^l$	liquid entropy outflow (J/K/s)
$\mathcal{S}^v$	vapor entropy outflow (J/K/s)
T	equilibrium temperature (K)
$V = (V_1, \dots, V_c, V_{H^v}))$	flash component and enthalpy vapor outflow (mol/s and J/s)
W	entropy production (potential) (J/K/s)
Greek symbols	
α_l, α_v	elements of $T\Sigma_M$ (mol and J)
μ^j_i	chemical potential of component i in phase j (J/mol)
Σ	equilibrium Riemannian manifold
τ^j	resident time in phase j (s)
$T\Sigma_M$	tangent space at $M \in \Sigma$
υ^j	volume function of phase j (m^3)
$\overline{\upsilon}^j$	flash volume of phase j (assumed constant) (m^3)
subscript 0	refers to initial conditions

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A Mathematical background

A.1 Euler identities for homogeneous functions of degree 1

The entropy S is an homogeneous function of degree 1, with respect to the extensive variables H et N: its successive derivatives obey Euler identities. Let f be a function of $x \in \mathbb{R}^n$, homogeneous of degree one. that is $f(\lambda x) = |\lambda| f(x)$. Then, its first and second derivatives obey:

$$\begin{array}{ll} Df(x).x = f(x), & Df(\lambda x) = Df(x), \\ D^2 f(x).(x, .) = 0, |\lambda| D^2 f(\lambda x) = D^2 f(x). & \end{array}$$

A.2 Riemannian manifold and gradient systems

A detailed presentation of Riemannian geometry can be found in Boothby's book (Boothby, 1975). An elementary introduction to gradient systems is sketched in the book of Hirsch and Smale, page 199 (Hirsch and Smale, 1974). We here recall the definition of the objects used in this paper. Our presentation can be made more rigorous if necessary. Consider Σ, a manifold of dimension n. Denote M the current point on Σ and $T\Sigma_M$, of dimension n, the tangent vector space to Σ at M. A **Riemannian metric** Q is characterized by an application $\Sigma \ni M \to Q_M$, where Q_M is a positive definite quadratic form on $T\Sigma_M$. Geometrically, $\sqrt{Q_M(u)}$ is the length of the tangent vector $u \in T\Sigma_M$. Q_M defines on $T\Sigma_M$ a unique scalar product denoted $< ., . >_M$, such that $< u, u >_M = Q_M(u)$ for every $u \in T\Sigma_M$.

The **gradient** of the real function W on Σ is the unique vector field

$$\Sigma \ni M \to \nabla W(M) \in T\Sigma_M$$

satisfying

$$\forall u \in T\Sigma_M, \quad < \nabla W(M), u >_M \quad = \quad L_u W(M),$$

where $L_u W$ is the Lie derivative of W with respect to u. $L_u W$ corresponds to the first variation of W in the tangent direction u at M. To every vector field $X \to X(M)$ corresponds a differential system $dM/dt = X(M)$. This system is called **gradient system** if, and only if, the vector field X is equal to the opposite of the gradient of a real function W: $X = -\nabla W$. W is called the **potential** of the system.