AIChE

Note on Flash and Distillation Systems

Mohit Aggarwal and B. Erik Ydstie
Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh PA 15213

DOI 10.1002/aic.14201

Flash and distillation systems evolving on the equilibrium manifold possess stable steady states when the molar flows and the boundary conditions are fixed and a vapor and liquid phase is present at all times. The results extend the range of validity of a local stability theorem for linear, constant molar overflow systems due to Acrivos and Amundson. The approach to stability analysis is motivated by the tangent plane method developed by Gibbs to open systems as it takes advantage of the negative curvature of the entropy surface to construct a Lyapunov function. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3322-3332, 2013
Keywords: thermodynamics, stability, Lyapunov function, convergence, distillation, process control

Introduction

"One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity."

J. W. Gibbs, American Scientist, 1839–1903.

More than 50 years ago, Acrivos and Amundson showed how matrix mathematics could be used for modeling, numerical simulation, and stability analysis of chemical process systems.[1] One application they studied concerned the stability of multicomponent distillation. They worked under the assumption of constant molar overflow (CMO) and equilibrium relations $y_i = K_i x_i$ with constant K_is. Under these conditions, the matrix differential equation for the system dynamics is linear and described by the system

$$\frac{dx}{dt} = Ax + b, \qquad x(0) = x_0 \tag{1}$$

The vector x consists of deviations in the liquid-phase mole-fractions from a given steady state, b is a vector of external perturbations, and the matrix A is given by the equilibrium relations. The authors went on to show that the eigenvalues of A are negative and real. It follows that the fixed point corresponds to a stable node and convergence toward the stationary point is nonoscillatory. However, the equilibrium relation is restrictive, as acknowledged by the authors, and the result does not go far in understanding how to design and operate distillation columns.

The next important breakthrough was provided by Rosenbrock. In 1962, he used Lyapunov's second method to prove that a binary distillation column has a stable steady state under the following assumptions: (1) constant molar overflow; (2) every vapor composition y_i corresponds to a unique liquid composition x_i; and (3) the stages are nonideal and approximated with Murphree efficiency.[2,3] The author commented that the method of analysis does not extend to multicomponent systems.

A decade later, Doherty and Perkins (DP) provided a critical review of the state-of-art in light of research that showed the existence of multiple steady states in distillation systems.[4] They concluded that a comprehensive theory for distillation systems was needed for process design and control. In the article, they reviewed different models and assumptions, they proposed a program for research and developed theory to show stability of continuous distillation of homogeneous mixtures. They concluded that the differential equations governing the dynamic behavior of a multicomponent distillation plate (a flash) possesses an asymptotically stable steady state*.

Sridhar and Lucia (SL) analyzed steady-state flash and distillation systems.[5,6] They showed that flash and distillation processes admit unique steady-state solutions without using CMO and simplified phase equilibrium. The convexity arguments used in their analysis are similar to the ones we use to prove stability. One difference being that that SL used the Gibbs free energy of the two phases as their point of departure, whereas we use the entropy of the overall system.

The next advance in stability analysis was made in 1993 when Rouchon and Cref (RC) demonstrated stability of the multicomponent flash under a set of conditions similar to those of DP. They fixed the feed-conditions, pressure, and the vapor and liquid volumes. The adiabatic case was studied and they showed that the multicomponent flash was stable.[7]

**Unfortunately, although the result is correct, the stability proof has a flaw. In a key step, it is claimed that* $\left(x_i - x_i^s\right)\left(y_i - y_i^s\right) > 0$*, that is,* $\delta x_i \delta y_i > 0$*, based on the following thermodynamic stability criterion for homogeneous mixtures:* $\left(\frac{\partial y_i}{\partial x_i}\right)_{P,x'} > 0$*. However,*

$$\delta x_i \delta y_i = \delta x_i \left(\frac{\partial y_i}{\partial x_1}\right)\delta x_1 + \delta x_i \left(\frac{\partial y_i}{\partial x_2}\right)\delta x_2 + \ldots +$$
$$\left[\delta x_i \left(\frac{\partial y_i}{\partial x_i}\right)\delta x_i\right] + \ldots + \delta x_i \left(\frac{\partial y_i}{\partial x_{c-1}}\right)\delta x_{c-1}$$

and we conclude that although the term between brackets in the above expression is positive, $\delta x_i \delta y_i$ *has an undefined sign.*

Correspondence concerning this article should be addressed to B. E. Ydstie at ydstie@cmu.edu.

It should be noted that RC did not treat the equilibrium flash.

Many articles have been published showing complex dynamics, such as bifurcations and sustained oscillation, in distillation systems. An early simulation result due to Magnussen, Michelsen, and Fredenslund showed the existence of three steady-state solutions in distillation of the ethanol-water-benzene azeotrope.[8] Multiple steady states in distillation were later confirmed experimentally in binary[9] and azeotropic distillation.[10]

Jacobsen and Skogestad[11,12] showed that multiplicities and instability may occur in binary distillation, especially when the internal flows are large. One source of multiplicity may occur when reflux is specified on mass or volumetric basis (rather than molar), even when one assumes CMO. Multiplicity and instability are likely to occur for mixtures with large differences in the component mole weights, for example, for the methanol-propanol system. Another source of multiplicity may occur when the reboiler duty is specified (rather than the molar vapor flow) and the lightest component has the largest heat of vaporization, for example, for the propanol-acetic acid system. For varying molar flows inside the column (not CMO), multiplicity and instability may occur even when reflux and vapor flow (boilup) are specified on a molar basis, for example, for the methanol-propanol system without the CMO assumption.

The stability analysis in our paper is based on the convergence theory introduced by Demidovich.[13] Convergence means that trajectories become closer and merge to a single trajectory. It follows that all converging systems are asymptotically stable, but not all asymptotically stable systems are converging.

Thermodynamic Foundations

We are concerned with the existence, uniqueness, and stability of solutions to a class of nonlinear dynamical systems with equilibrium constraints. The state of the system is given by the vector

$$Z=(U,V,N_1,\dots,N_{n_c})^T \tag{2}$$

The components of the vector Z are thereby identified with extensive variables such as the internal energy, volume, and mole numbers of n_c chemical species. Associated with every state Z, we have a vector of conjugate or intensive variables

$$w(Z)=\left(\frac{1}{T},\frac{P}{T},-\frac{\mu_1}{T},\dots,-\frac{\mu_{n_c}}{T}\right)^T \tag{3}$$

where T is the temperature, P the pressure, and μ_j the chemical potential of component j at Z. We denote the space of extensive variables $\mathbb{Z}$ and the space of intensive variables $\mathbb{W}$. With these abstractions, we now define what is meant by a multiphase equilibrium system.[14,15]

Definition 1. *A composite system consisting of two constituent subsystems with states Z_1 and Z_2 are in thermodynamic equilibrium if and only if $w_1=w_2$. Two subsystems in thermodynamic equilibrium, equilibrium for short, are distinguishable if their states are linearly independent, that is, $Z_1 \neq \lambda Z_2$ for any positive scalar λ. Consider now a composite system that consists of n subsystems that are all in equilibrium with each other. We denote the states of the subsystems by $Z_i, i=1,\dots,n$. The composite system is said to have n_p phases if there are n_p distinguishable subsystems. The state of the thermodynamic system is given by $Z=Z_1+,\dots,+Z_n$.*

Feinberg[15] shows that the construction given above limits the number of possible states so that $1 \le n_p \le n_c+1$, a property that is referred to as Gibbs phase rule. The phase equilibrium problem can now be stated in a general form suitable for stability analysis and control design.

The phase-distribution problem

Given the state Z of a composite system find the number of phases n_p and the phase-distribution, that is, the maximum number of linearly independent vectors Z_i so that

$$Z=\sum_{i=1}^{n_p} Z_i \tag{4}$$

$$0=w_i-w_j, \qquad \text{for all pairs } 1 \le i,j \le n_p \tag{5}$$

The first equation expresses additivity of the extensive variables and the second equation shows that the temperature, pressure, and chemical potentials are the same in all phases.

The existence and uniqueness of the solution to the problem above is dealt with in texts on thermodynamics such as Callen.[14] However, the phase-equilibrium problem is not usually solved in the form stated here as the functions $w(Z)$ are not normally known explicitly. In numerical simulation studies, it is more often convenient to fix T and P instead of U and V. Efficient numerical methods have been developed for such cases, especially for two-phase, vapor-liquid equilibrium problems.[5,8,16–18]

The entropy of the equilibrium system is defined so that

$$S=\frac{1}{T}U+\frac{P}{T}V-\sum_{j=1}^{n_C}\frac{\mu_j}{T}N_j \tag{6}$$

The entropy defines a surface in the n_c+3 dimensional space of the thermodynamic variables $S,U,V,N_1,\dots,N_{n_c}$ called the equilibrium manifold. The example shown in Figure 1 represents the entropy of a water-like substance with fixed mole numbers. The surface is smooth with concave and convex subregions. The convex regions are not physically accessible. Concave regions below the concave envelope (not shown) represent metastable states that are physically accessible but do not correspond to entropy maximization.

In our compact notation, we have

$$S=w^TZ$$

By differentiating, we find $dS=w^TdZ+Z^Tdw$. The latter term vanishes due to the homogeneous degree one property of the entropy. This is the Gibbs–Duhem equation and we get the identity

$$\frac{\partial S}{\partial Z}\equiv w^T$$

The intensive variables are therefore tangent to the equilibrium manifold. By taking second derivatives, we find the local curvature of the equilibrium manifold

$$M(Z)=\frac{\partial w(Z)}{\partial Z}\le 0$$

The curvature is nonpositive due to the concavity of S. However, the equilibrium surface is not strictly concave and M is therefore semidefinite. The number of phases at a point $Z \in \mathbb{Z}$ is related to the rank deficiency of M so that

$$n_p(Z)=2+n_c-\text{rank}\,(M(Z)) \tag{7}$$

To see how this comes about consider the variation of w at the point Z defined so that

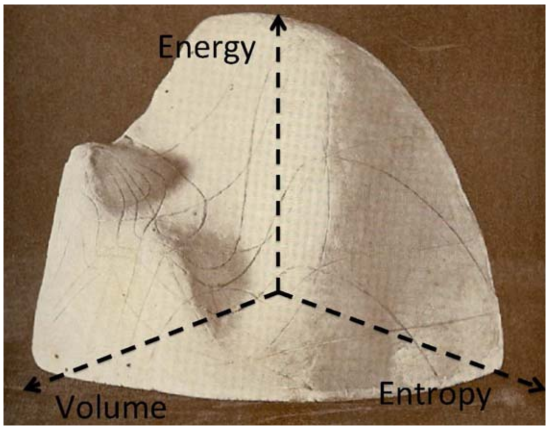


Figure 1. The equilibrium surface of water shown here was based on data published by Joshua Willard Gibbs in 1973.

The Scottish Physicist J.C. Maxwell sculpted the original model in clay in the Cavendish Laboratory at Cambridge University in 1874 and offered it to Gibbs as a gift. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\delta w = M \delta Z \tag{8}$$

A variation $\delta Z = Z - Z_1$ is defined as a "virtual" change where Z is considered fixed and Z_1 is allowed to vary.

The homogeneous degree one property implies that we can scale the state of the system with a positive constant without changing the intensive variables so that $w(\lambda Z) = w(Z)$. This means that w is homogenous degree zero and we conclude from Eq. 8 that rank(M) $\leq n_c + 1$ for all $Z \in \mathbb{Z}$. It follows that the equilibrium manifold is bounded by a cone. This does not show up in Figure 1 because Maxwell fixed the mole numbers to allow the three-dimensional representation.

Definition 1 shows that there may exist nonempty subsets $Z_i \in \mathbb{Z}$ where the degeneracy of M is higher than one. In regions where two phases coexist, two linearly independent vectors Z_1 and Z_2 scale so that $w(\lambda_1 Z_1 + \lambda_2 Z_2) = w(Z_1 + Z_2)$ for all positive scalars λ_1, λ_2. This means that we can scale the size of each phase independently without changing the intensive variables. We therefore find that rank(M) $= n_c$ for a two phase system etcetera for systems with three or more phases. Thus, we can view the rank deficiency of M at a given point $Z \in \mathbb{Z}$ as a definition of how many phases there are present in a mixture as seen in Eq. 7.

Because M is rank-deficient of degree n_p, we cannot use M to define a norm for the space $\mathbb{Z}$ as in Riemannian geometry. However, M can be used to define a norm for the space $\mathbb{W}$. Let

$$W(Z, \delta Z) = -\delta Z^T M(Z) \delta Z = -\delta Z^T \delta w \tag{9}$$

We then have according to the discussion above

1. $W(Z, \delta Z) \geq 0$, nonnegativity
2. $W(Z, \delta Z) = 0$ if and only if $\delta w = 0$, coincidence

We also have positive constants $\epsilon_1 \leq \epsilon_2$ so that

$$\epsilon_1 ||\delta w(Z)||^2 \leq W(Z, \delta Z) \leq \epsilon_2 ||\delta w(Z)||^2$$

It follows immediately that (See Appendix A)

$$W(Z, \delta Z) = -\delta^2 S(Z) \tag{10}$$

Our approach to stability analysis therefore follows the following pattern. First, generate the entropy balance for the system. Second, calculate the second variation of the entropy. Third, establish if W converges. If it does, then the intensive variables converge to a single trajectory.

The norm W can be augmented to define a norm for $\mathbb{Z}$ by adding a matrix that spans directions not accounted for by M. Many possibilities exist, the simplest consists of adding a symmetric matrix $K_c(Z)$ with rank$(K_c) \geq n_p$ and define

$$W(Z, \delta Z) = \delta Z^T (K_c(Z) - M(Z)) \delta Z \tag{11}$$

W now measures the distance between the points Z and Z_1 provided K_c is chosen so that $K_c - M$ is positive definite at Z.

Another important concept we is the idea of a thermodynamic process. A process moves a thermodynamic system from a state Z_1 to another state Z_2 by adding heat, material, or by compression. Such a process may be adiabatic, isothermal, or isobaric. It may be open or closed and it may follow any number of different paths. Regardless of how the process is carried out, we find that the intensive variables change according to the formula[19]

$$w(Z_1) - w(Z_2) = \Pi(Z_1, Z_2)(Z_1 - Z_2) \tag{12}$$

where

$$\Pi(Z_1, Z_2) = \int_0^1 M(\epsilon Z_2 + (1-\epsilon) Z_1) d\epsilon$$

More details are provided in Appendix A and many examples of simple processes are given in the books by Callen[14] and Sandler.[20]

The Equilibrium Flash

The model for the equilibrium flash shown in Figure 2 is developed under the assumptions that the total volume is constant and that vapor and liquid phases are present at all times. The inventories U, V, N are time varying and evolve according to the differential constraints

$$\begin{aligned} \frac{dU}{dt} &= F h_F - D h_D - L h_L + Q, \\ \frac{dV}{dt} &= 0 \\ \frac{dN_i}{dt} &= F z_i - D y_i - L x_i \qquad i = 1 \ldots n_c \end{aligned} \tag{13}$$

The variables h_F, h_D, h_L are the molar enthalpies of the feed, the distillate, and the liquid products, Q the heat input, F, D, and L represent the molar flow rates of the feed, distillate, and liquid products, respectively, and z_i is the mole fraction of component i in the feed. The vapor and liquid mol fractions are defined so that

$$y_i = N_{Vi} / N_V, \; x_i = N_{L,i} / N_L \tag{14}$$

where N_V and N_L are the vapor and liquid molar hold-ups, respectively.

The problem we consider concerns the issue of whether or not the state of the flash converges when the boundary conditions are fixed. Many different possibilities exist. We consider the case when the outlet molar flows and the inlet conditions are fixed. The more general problem, which we

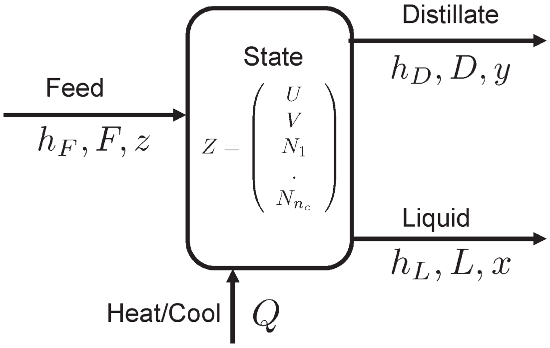


Figure 2. The flash system.

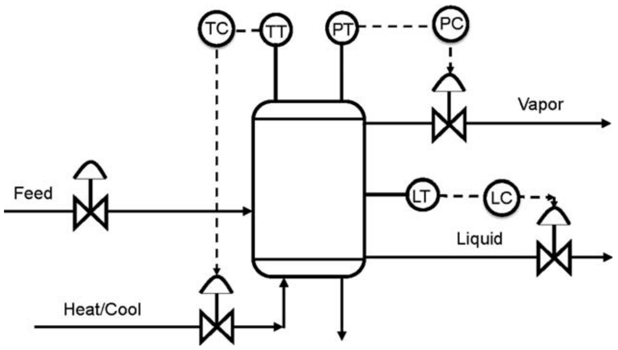


Figure 3. The flash with temperature, pressure, and liquid level feedback controls.

do not consider in this article, could include the dynamics of control systems.

The differential system (13) is solved from initial conditions $\{U(0), V(0), N_i(0), i=1, \ldots, n_c\}$ subject to the equilibrium and mass balance constraints (4) and (5) with $n_p=2$ so that

$$Z = Z_V + Z_L \tag{15}$$

$$0 = w_V - w_L \tag{16}$$

The differential algebraic equation (DAE) system (13–16) has n_c+2 differential constraints, $5n_c+10$ algebraic constraints, and the $8n_c+17$ variables seen in Table 1. The remaining n_c+5 variables are fixed by boundary conditions and controls.

A practical control system for the flash is shown in Figure 3. In this set up, there is one controller for the liquid flow, a temperature controller to manage the energy balance, and a pressure controller to manage the vapor hold-up. The liquid flow controller can, for example, be derived from the total mol balance

$$\frac{dN}{dt} = F - D - L \tag{17}$$

The objective is to choose a feedback control strategy to keep the total mole number N constant and equal to a setpoint N_0. The inventory control strategy

$$L = F - D + K_1(N_0 - N) \tag{18}$$

where K_1 is the controller gain, achieves this objective. Substituting the control (18) into the mole balance (17) gives

$$\frac{dN}{dt} = K_1(N_0 - N)$$

so that N converges to N_0 with convergence rate K_1^{-1}. In the limit, we get the steady state balance

$$F = V + D \tag{19}$$

Other types of control systems can be developed to achieve other objectives, such as constant temperature and pressure or concentration of a specific component or stripping factor. In simulation, dynamic controllers are often ignored and they are simply assumed to work as desired by fixing variables such as temperature and pressure stripping factors. Some care has to be taken as the index of the DAE system may increase when constraints are imposed.

Table 1. Variables in the Flash Systems

	Variables	Number
Controls	D, L, Q	3
Disturbances	z, h_f, F	n_c+2
Latent	$Z, Z_L, Z_V, x, y, h_D, h_L$	$7n_c+12$
Total		$8n_c+17$

The dynamic system (13) with algebraic constraints (14–16) and control (18) has index equal to one. Such constraints are referred to as holonomic constraints in classical mechanics. The implicit function theorem guarantees that they can be removed and the flash system can be described by a system of nonlinear differential equations on the form

$$\frac{dZ}{dt} = f(Z) + b, \; Z(0) = Z_0 \tag{20}$$

where f is the drift and b is a function of the boundary conditions and controls. It was shown by Acrivos and Amundson that the linearized distillation system can be written like so when the equilibrium relations are constant.[1] RC[7] use geometric control theory to show that higher-order constraints also can be removed so that system (20) can be developed from Eq. 13–16 with constant pressure and temperature conditions.

Stability of the Flash

We will use the norm $W(Z, \delta Z)$ in Eq. 11 as a control-Lyapunov function (CLF) to analyze the stability of the flash system. W is called a CLF as it includes degrees of freedom to be determined by controls and boundary conditions. It is convenient to use

$$W = -\delta Z^T M(Z) \delta Z + \underbrace{K_1(V - V_0)^2 + K_2(N - N_0)^2}_{\text{Controls}} \tag{21}$$

in the stability analysis, The scalars K_i are positive. V_0 denotes the reference value for the total volume and N_0 denotes the reference value for the total mole number. These latter terms vanish when the volume and total molar hold-up are constant.

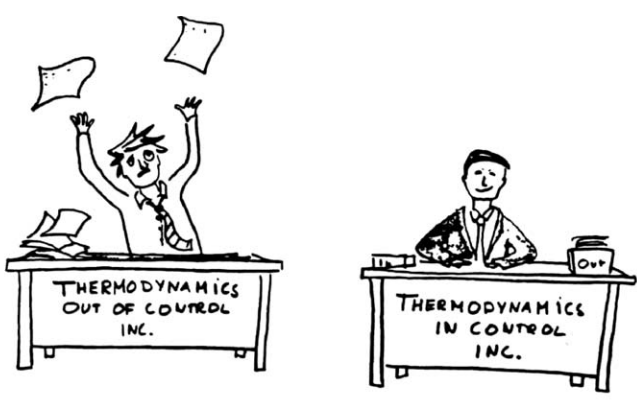
In the next stage of the development, we need to show that $\epsilon_0 > 0$ exists so that

$$\frac{dW}{dt} \leq -\epsilon_0 W \tag{22}$$

W then converges to zero exponentially. This implies that we can write

$$||\delta Z(t)|| \leq \exp\left(-2\epsilon_0 \lambda_{\min} t\right) ||\delta Z(0)||$$

where $\lambda_{\min}$ is the minimum eigenvalue of the matrix $-M + K_c$, that is



Copyright @ B E Ydstie

Figure 4. Thermodynamics provides an organized way to model and analyze the stability of chemical engineering process systems.

$$\lambda_{\min}=\inf_{i,t}\ \lambda(-M+K_c), \qquad i=1,\dots,n_c+2$$

Trajectories then converge to a single trajectory and convergence theory establishes existence, uniqueness, and stability of the solutions to the differential equations describing the system dynamics.[13,21,22] As we will see, the thermodynamic perspective provides an organized way of deriving the sufficient conditions needed to establish inequality (22) (Figure 4).

Combining the differential constraints (13) with definition (6) gives the entropy balance (See Appendix B)

$$\frac{dS}{dt}=\underbrace{S_F-S_D-S_L+\frac{Q}{T_0}}_{\text{Entropy flux - }\phi_S}+\underbrace{A_F+F\frac{\hat{V}}{T}(P_F-P)+Q\left(\frac{1}{T}-\frac{1}{T_0}\right)}_{\text{Entropy Production - }\sigma_S} \tag{23}$$

Here, we use the notation $S_F=w_F^TZ_F, S_D=w^TZ_D, S_L=w^TZ_L$, where Z_F,Z_D,Z_L denote the vector of flows of storage variables, for example, $Z_F^T=F\left(\hat{U},\hat{V},\hat{N}_1,\dots,\hat{N}_{n_c}\right)_F$. The temperature scaled availability is defined so that

$$A_F=(w-w_F)^T\,Z_F=w^TZ_F-S(Z_F)\geq 0 \tag{24}$$

Differentiating Eq. 21 gives

$$\frac{dW}{dt}=-\delta^2\left(\frac{dS}{dt}\right)+\frac{dW_c}{dt}$$

where we have ignored terms of order three and higher and

$$W_c=K_0(V-V_0)^2+K_1(N-N_0)^2$$

The entropy balance (23) provides the following expression for the CLF

$$\frac{dW}{dt}=\underbrace{-\delta^2\left(S_F-S_D-S_L+\frac{Q}{T_0}\right)}_{\text{Entropy Flux}}$$
$$\underbrace{-\delta^2\left(A_F+F\frac{\hat{V}}{T}(P_F-P)-Q\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}_{\text{Dissipation}}+\underbrace{\frac{dW_c}{dt}}_{\text{Controls}} \tag{25}$$

Expression (25) holds for any constant volume flash provided the operations of differentiation and second order variation commute. This is the case if the total molar flows are constant, the vapor and liquid molar hold-ups are constant and the heating rate is constant. We now develop two stability results for different boundary conditions.

Theorem 1. *Adiabatic Flash: Suppose that the heating rate Q is constant, the state of the incoming fluid $\hat{Z}_F^T=\left(\hat{U}_F,\hat{V}_F,\hat{N}_1,\dots,\hat{N}_{F,n_c}\right)$ and the molar flows F,D,L are constant and in balance so that*

$$F=D+L$$

The state Z then converges to a unique, stationary steady state provided Eq. 25 holds.

Proof. We first insert definition (24) into Eq. 25 to give

$$\frac{dW}{dt}=\delta^2\left(S_{\mathrm{D}}+S_{\mathrm{L}}-\frac{Q}{T_0}\right)$$
$$+\delta^2\left(\underbrace{w^TZ_F}_{1}+\underbrace{F\hat{V}\frac{P_F}{T}}_{2}-\underbrace{F\hat{V}\frac{P}{T}}_{3}-\underbrace{Q\left(\frac{1}{T}-\frac{1}{T_0}\right)}_{4}\right)+\frac{dW_c}{dt} \tag{26}$$

To complete the development, it useful to note that the specific volume

$$\hat{V}=V_0/N_0=\text{a constant}$$

as the total volume and the molar hold-up are constant. We now show that the terms 1–4 in Eq. 26 vanish.

Term 1:

$$\delta^2\left(w^TZ_F\right)=\delta^2(w)Z_F=0$$

Here, we used the facts that Z_F is constant and $\delta^2w=0$.

Term 2:

$$\delta^2\left(\hat{V}\frac{P_F}{T}\right)=\delta\left(\frac{P_F}{T}\delta\hat{V}+\hat{V}\delta\left(\frac{P_F}{T}\right)\right)=0$$

here we used the fact that $\hat{V}$ is constant so that $\delta\hat{V}=0$. We also used the fact that $\delta^2(P_F/T)=0$.

Term 3: In the same way

$$\delta^2\left(\hat{V}\frac{P}{T}\right)=\delta\left(\frac{P}{T}\delta\hat{V}+\hat{V}\delta\left(\frac{P}{T}\right)\right)=0$$

Term 4: And finally

$$\delta^2\left(Q\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)=0$$

as Q is constant and $\delta^2(1/T)=0$ and $\delta^2(1/T_0)=0$ as T_0 is constant.

We have $dW_c/dt=0$ as the equality $F=L+V$ gives $dN/dt=0$ and $N=N_0$ for all $t\geq 0$. Combining these results gives

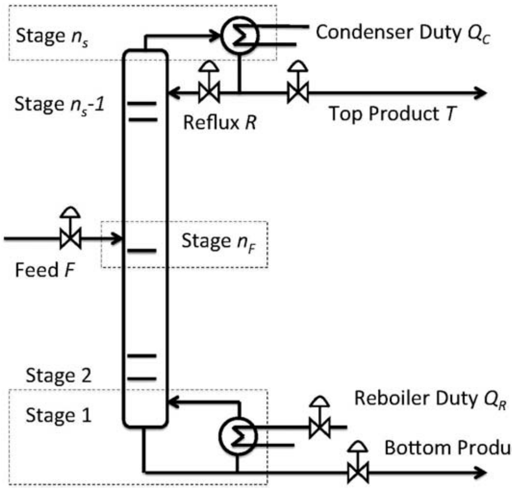


Figure 5. A simple distillation column.

$$\frac{dW}{dt}=\delta^2\left(D\hat{S}_V\right)+\delta^2\left(L\hat{S}_L\right)$$
$$\leq \delta^2\left(\frac{D}{N_V}N_V\hat{S}_V\right)+\delta^2\left(\frac{L}{N_L}N_L\hat{S}_L\right)$$

Hence

$$\frac{dW}{dt}=\delta^2\left(\frac{D}{N_V}S_V\right)+\delta^2\left(\frac{L}{N_L}S_L\right) \qquad (27)$$

Define $\epsilon_1=\min\{D/N_V, L/N_L\}$ and use the fact that $S=S_V+S_L$ and we can write

$$\frac{dW}{dt}\leq\frac{\epsilon_1}{N}\delta^2S=-\frac{\epsilon_1}{N}W \qquad (28)$$

Inequality (22) is now established with $\epsilon_0=\epsilon_1/N$. ☐

The result shows that the exponential convergence rate is bounded by

$$\epsilon_1=\min\{D,L\}\frac{1}{N}$$

A high convergence rate is achieved when the residence time is small. The estimate tends to zero as either the liquid or the vapor rate decrease to zero.

Theorem 2. *Isothermal and/or isobaric flash stability: Suppose that the pressure P and/or temperature T are constant, the state of the incoming fluid $\hat{Z}_F$ and the molar flows F, D, L are constant with $F=D+L$. The state Z then converges to a unique, stationary steady state provided Eq. 25 holds.*

Proof. In this case, we insert the constant pressure and temperature conditions into the proof and the same result follows. ☐

We relied extensively on the concavity and differentiability of the entropy function. The concavity is derived from the second law as shown in Appendix A. In a metastable system, there may be ambiguity in the number of phases. Infinitesimal perturbations or a spontaneous fluctuation can lead to a finite perturbation when the vapor is subcooled or the liquid is superheated.

Stability of Distillation Columns

We consider again the separation of a multicomponent mixture, but now in a distillation column with stages as shown in Figure 5. Stage 1 corresponds the reboiler and stage n_s corresponds to the condenser. For stages $n=1,\ldots,n_s$, we have energy and material balances given by the mesh equations

$$\frac{dU_n}{dt}=F_nh_{F,n}+L_{n+1}h_{L,n+1}+D_{n-1}h_{D,n-1}-L_nh_{L,n}-D_nh_{D,n}+Q_n$$
$$\frac{dV_n}{dt}=0$$
$$\frac{dN_{n,i}}{dt}=F_nz_{n,i}+L_{n+1}x_{n+1,i}+D_{n-1}y_{n-1,i}-L_nx_{n,i}-D_ny_{n,i},\quad i=1\ldots n_c \qquad (29)$$

The notation is the same as for the flash and further explained in Figure 6 for the generic tray n.

We assume that there is one feed tray (Stage n_F) so that

$$F_n=0\quad\text{for } n\neq n_F, F_{n_F}=F$$

For the condenser (Stage n_s in Figure 5), we have

$$D_{n_s}=L_{n_s+1}=0,\ L_{n_s}=R+T$$

The reboiler (Stage 1 in Figure 5) is modeled so that

$$D_0=0,\ L_1=B$$

The heat-duties are equal to zero except Stage 1 (reboiler) and Stage n_s (condenser) so that

$$Q_n=0,\ \text{for } n\neq 1, n_s,\ Q_1=Q_R,\ Q_{n_s}=Q_C$$

Example: *Distillation with two trays: To introduce the application of the stability theory, we consider first distillation with two stages as seen in Figure 7. The column has a feed, a liquid draw from the bottom and a vapor draw from the top.*

The entropy balance for Stage 1 is given by

$$\frac{dS_1}{dt}=F\hat{S}_F-D_1\hat{S}_{D,1}+L_2\hat{S}_{L,2}-L_1\hat{S}_{L,1}+\frac{Q_B}{T_B}$$
$$+F\left(\hat{A}_F+\frac{\hat{V}_1}{T_1}(P_F-P_1)\right)+L_2\left(\hat{A}_L+\frac{\hat{V}_1}{T_1}(P_2-P_1)\right)$$
$$+Q_B\left(\frac{1}{T_1}-\frac{1}{T_B}\right)$$

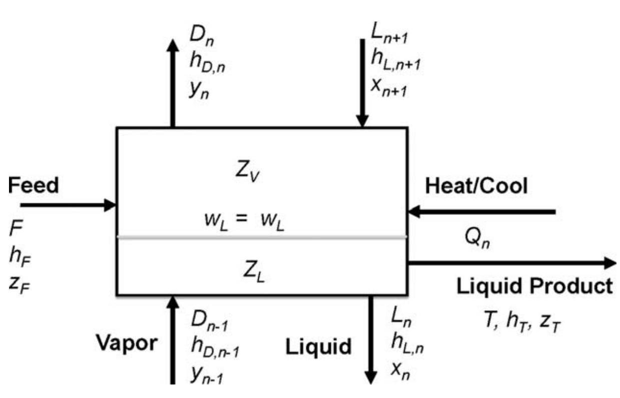


Figure 6. Tray *n* in the distillation column.

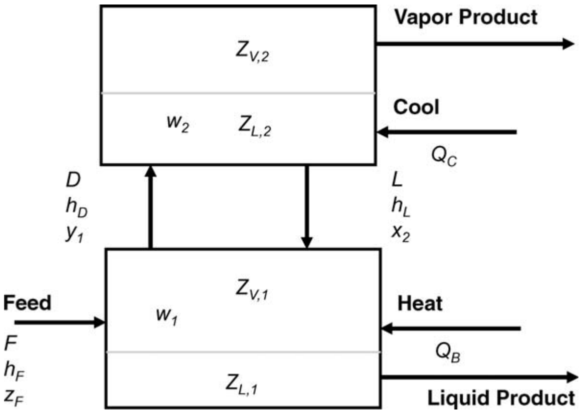


Figure 7. Two-stage distillation column.

The first line describes the rate of entropy flux to and from Stage 1. The second line describes the rate of dissipation due to mass transfer and fluid flow and the last line describes the rate of dissipation due to heat transfer from the reboiler. A similar equation for Stage 2 yields

$$\begin{aligned}\frac{dS_2}{dt}=&D_1\hat{S}_{V,1}-L_2\hat{S}_{L,2}-D_2\hat{S}_{v,2}+\frac{Q_C}{T_C}\\&+D_1\left(\hat{A}_D+\frac{\hat{V}_2}{T_2}(P_1-P_2)\right)\\&+Q_C\left(\frac{1}{T_2}-\frac{1}{T_C}\right)\end{aligned}$$

By adding the two equations, we find that the overall entropy balance

$$\begin{aligned}\frac{dS}{dt}=&F\hat{S}_F-L_1\hat{S}_{L,1}-D_2\hat{S}_{D,2}+\frac{Q_B}{T_B}+\frac{Q_C}{T_C}\\&+F\left(\hat{A}_F+\frac{\hat{V}_1}{T_1}(P_F-P_1)\right)+D_1\left(\hat{A}_D+\frac{\hat{V}_2}{T_2}(P_1-P_2)\right)\\&+L_2\left(\hat{A}_L+\frac{\hat{V}_1}{T_1}(P_2-P_1)\right)\\&+Q_B\left(\frac{1}{T_1}-\frac{1}{T_B}\right)+Q_C\left(\frac{1}{T_2}-\frac{1}{T_C}\right)\end{aligned}\tag{30}$$

where $S=S_1+S_2$ is the sum of the entropies of the two stages. The three availabilities are defined so that

$$\hat{A}_F=(w_1-w_{\mathrm{F}})^T\hat{Z}_F$$
$$\hat{A}_D=(w_2-w_1)^T\hat{Z}_{D,1}$$
$$\hat{A}_L=(w_1-w_2)^T\hat{Z}_{L,2}$$

The dissipation terms combine so that

$$D_1\hat{A}_{D,}+L_2\hat{A}_{L,}=-(w_1-w_2)^T\left(D_1\hat{Z}_{D,1}-L_2\hat{Z}_{L,2}\right)\tag{31}$$

From Eq. 12, we have the process

$$(w_1-w_2)=\Pi(Z_1,Z_2)(\lambda_1Z_1-\lambda_2Z_2)$$

for any λ_1,λ_2 positive. This equation describes how the intensive variables change as a function of the extensive variables. The independence of λ_i follows from the homogeneous degree zero property of the intensive variables. We can now write

$$D_1\hat{A}_D+L_2\hat{A}_L=\left(Z_{D,1}-Z_{L,2}\right)^T\Pi\left(Z_{D,1}-Z_{L,2}\right)$$

where $Z_{D,1}=D_1\hat{Z}_{D,1}$ etcetera. We can, therefore, rewrite the entropy balance in its final form for our purposes so that

$$\begin{aligned}\frac{dS}{dt}=&F\hat{S}_F-L_1\hat{S}_{L,1}-D_2\hat{S}_{D,2}+\frac{Q_B}{T_B}+\frac{Q_C}{T_C}\\&+F\hat{A}_F+F\frac{\hat{V}_1}{T_1}(P_F-P_1)+D_1\frac{\hat{V}_2}{T_2}(P_1-P_2)+L_2\frac{\hat{V}_1}{T_1}(P_2-P_1)\\&-\left(Z_{D,1}-Z_{L,2}\right)\Pi\left(Z_{D,1}-Z_{L,2}\right)+Q_B\left(\frac{1}{T_1}-\frac{1}{T_B}\right)-Q_C\left(\frac{1}{T_2}-\frac{1}{T_C}\right)\end{aligned}\tag{32}$$

The first line represent entropy flow. The next represents entropy production due to compression and viscous dissipation. The last two lines represent entropy production due to mass and energy exchange between stages and heat exchange with the environment. All these terms contribute to positive entropy production.

Taking the second variation (assuming that the differentiation and the second variations commute) and eliminating terms that are equal to zero gives the much simpler expression

$$\frac{d}{dt}\delta^2S=-L_2\delta^2S_{L,1}-D_1\delta^2S_{D,2}-\delta^2\left(\left(Z_{D,1}-Z_{L,2}\right)\Pi\left(Z_{D,1}-Z_{L,2}\right)\right)$$

Now

$$\delta^2\left(\left(Z_{D,1}-Z_{L,2}\right)\Pi\left(Z_{D,1}-Z_{L,2}\right)\right)=\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Pi\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Big)$$

Using the identity $W_i=-\delta^2S_i$, we get

$$\frac{dW}{dt}=-L_1W_{L,1}-D_2W_{D,2}-\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Pi\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Big)$$

We can rearrange the expression and write the integral

$$\begin{aligned}W(t)-W(0)=\int_0^t&-L_1W_{L,1}-D_2W_{D,2}\\&-\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Pi\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\end{aligned}$$

Since $W(t)\geq 0$, we conclude

$$\int_0^\infty L_1W_{L,1}+D_2W_{D,2}\leq W(0)$$
$$\int_0^\infty\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Pi\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\leq W(0)$$

It follows from continuity that that

$$\lim_{t\to\infty}W_{L,1}=0$$
$$\lim_{t\to\infty}W_{D,2}=0$$
$$\lim_{t\to\infty}\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)\Pi\left(\delta^2Z_{D,1}-\delta^2Z_{L,2}\right)=0$$

From the first two equations, we can conclude that w_1 and w_2 converge to stationary values. From the second equation, we conclude that interstage variations converge so that

$$\lim_{t\to\infty}(\delta w(i)-\delta w(i+1))=0,\qquad i=1,\ldots,n_s-1$$

But, w_1 and w_{n_s} are constant in the limit so that means that all stages also converge.

The theory developed above generalizes quite easily to more general distillation systems. We make the assumption that liquid (L) and vapor (D) flows in the rectifying and the stripping sections are time-invariant (not necessarily the same from one stage to the next). We furthermore assume that the molar flows are balanced so that the overall mole balance is kept invariant for every tray, that is

$$F_n+L_{n+1}+D_{n-1}=L_n+D_n \quad \text{for } n=1,\ldots,n_s$$

hence

$$\frac{dN_n}{dt}=0$$

We can then conclude that the total volume V and the total molar hold-up on every tray are constant. Two independent extensive quantities are then fixed and it suffices to show convergence of the intensive properties. The approach is equivalent to the two stage system so we only give the outline of the proof.

Theorem 3. *Consider a distillation column where*

1. The molar flows are time-invariant and balanced as described above.
2. The reboiler heating rate Q_R and temperature T_R, the condenser cooling rate Q_C and temperature T_C are time-invariant.
3. The feed rate F and its state $\hat{Z}_F^T=(\hat{U}_F,\hat{V}_F,\hat{N}_1,\ldots,\hat{N}_{F,n_c})$ are time-invariant.

The states $Z_n, n=1,\ldots,n_s$ *of all stages then converge to a unique steady state provided time-differentiation and second variation commute and all internal flow rates as well as the distillate and bottoms rate are nonzero and positive.*

Proof. We first develop the entropy balance for every stage and then we apply the assumptions that provide constant hold-up and flows. Calculating the second variation for every stage and summing over the entire columns yields

$$\frac{d}{dt}\delta^2 S=-L_1\delta^2 S_{L,1}-D_{n_s}\delta^2 S_{L,n_s} - \sum_{i=1}^{n_s-1}\delta^2\left(\left(Z_{D,i}-Z_{L,i+1}\right)Q\left(Z_{D,i}-Z_{L,i+1}\right)\right)$$

From this we point, we apply the same approach as for the two stage system. ☐

Our analysis for multicomponent distillation, like that of Acrivos and Amundson, shows that persistent instabilities and multiplicities in distillation cannot occur when the heating rates and all internal flows are.

Conclusions and Brief Discussion

In this article, we studied the stability of multicomponent flash and distillation systems operating under adiabatic or isothermal and isobaric conditions. The results confirm previous results that demonstrate that multicomponent flash systems cannot exhibit complex behavior, that is multiple steady states and oscillations, when the inlet conditions are fixed and the molar flow rates are fixed. One question that remains open is to establish conditions under which the commutation in Eq. 25 holds. The Acrivos–Amundson article on matrix analysis provided a point of departure for our developments and in the spirit of this special issue we wanted to stay close to the original developments while relaxing the condition $y_i=K_ix_i$ with K_i constant. We therefore kept the assumption that flow rates are constant and balanced and that the feed conditions are time-invariant. Using these assumptions, we showed exponential stability of the flash system and asymptotic stability of the distillation system. Future research should aim to replace restrictive assumption on the hydrodynamics by including weir-equations and controls. It is important to develop a tighter analysis that provide exponential rather than asymptotic stability for distillation and include models for the hydrodynamics and control systems to compare the stability results with simulation and experimental results that show instability.

Acknowledgments

The research was supported by ALCOA Inc., under the New Generation Aluminum Production (NGAP) project and the National Science Foundation under CBET (0932556). We acknowledge the work of Mr. Felipe Tavares, Drs. Chad Farschman, Duncan Coffey, and Yuan Xu who all contributed in significant ways to the stability theory. We also appreciate very much the support and encouragement of Profs. Peter Monson of UMass Michael Doherty and Scott Shell of UCSB and very helpful comments from the reviewers.

Literature Cited

1. Acrivos A, Amundson NR. Application of matrix mathematics to chemical engineering problems. *Ind Eng Chem.* 1995;47:1533–1541.
2. Rosenbrock HHA. Theorem of dynamic conversion for distillation. *Trans Inst Chem Eng.* 1960;38:279–287.
3. Rosenbrock HHA. Lyapunov function with applications to some nonlinear physical problems. *Automatica.* 1962;1:31–53.
4. Doherty MF, Perkins JD. On the dynamics of distillation processes–iv uniqueness and stability of the steady state in homogeneous continuous distillations. *Chem Eng Sci.* 1982;37(3):381–392.
5. Sridhar LN, Lucia A. Analysis and algorithms for multistage separation processes. *Ind Eng Chem Res.* 1989;28(6):793–803.
6. Lucia A. Uniqueness of solutions to single-stage isobaric flash processes involving homogeneous mixtures. *AIChE J.* 1986;32(11):1761–1770.
7. Rouchon P, Creff Y. Geometry of the flash dynamics. *Chem Eng Sci.* 1993;48(18):3141–3147.
8. Magnussen T, Michelsen ML, Fredenslund A. Azeotropic distillation using UNIFAC. *Chem Eng Symp Ser.* 1979;56:1–19.
9. Kienle A, Groebel M, Gilles ED. Multiple steady states in binary distillation-theoretical and experimental results. *Chem Eng Sci.* 1995; 50:2691–2703.
10. Güuttinger TE, Dorn C, Morari M. Experimental study of multiple steady states in homogeneous azeotropic distillation. *Ind Eng Chem Res.* 1997;36:794–802.
11. Jacobsen EW, Skogestad S. Multiple steady states in ideal two-product distillation. *AIChE J.* 1991;37:499–511.
12. Jacobsen EW, Skogestad S. Instability of distillation columns. *AIChE J.* 1994;40(9):1466–1478.
13. Demidovich BP. Dissipativity of a nonlinear system of differential equations. 1961;Part I-6:19–27, 1962;Part II-1:3–8.
14. Callen HB. Thermodynamics, an Introduction to Thermostatics, 2nd ed. John Wiley & Sons, Inc., Hoboken, NJ, 1985.
15. Feinberg M. On Gibb's phase rule. *Arch Ration Mech Anal.* 1979; 70:219–234.
16. Michelsen ML. The isothermal flash problem: part ii phase split calculation. *Fluid Phase Equlib.* 1982;9:21–40.
17. McDonald CM, Floudas CA. Global optimization and analysis for the Gibbs free energy function using the UNIFAC, Wilson, and ASOG equations. *Ind Eng Chem Res.* 1995;34:1674–1687.

18. Xua G, Haynes WD, Stadtherr MA. Reliable phase stability analysis for asymmetric models. *Fluid Phase Equilib.* 2005;235:152–165.
19. Alonso AA, Ydstie BE, Stabilization of distributed systems using irreversible thermodynamics. *Automatica*. 2001;37:1739–1755.
20. Sandler S. Chemical, Bio-chemical and Engineering Thermodynamics. John Wiley & Sons, Inc., Hoboken, NJ, 2006.
21. Lohmiller W, Slotine JJE. On contraction analysis for non-linear systems. *Automatica.* 1998;34(6):683–696.
22. Pavlov A, Pogromsky A, van de Wouw N, Nijmeijer H. Convergent dynamics, a tribute to Boris Pavlovich Demidovich. *Syst Control Lett.* 2004;52:257–261.
23. Wightman A. Convexity and the notion of equilibrium state in thermodynamics and statistical mechanics, In: Introduction to R. B. Israel, Convexity in the Theory of Lattice Gases. Princeton, NJ: Princeton University Press, 1979.
24. Evans LC. Entropy and partial differential equations. Lecture notes from the Dpartment fo Mathematics, University of California, Berkeley, math.berkeley.edu/~evans/entropy.and.PDE.pdf, 2008.
25. Glansdorff P, Prigogine I. Thermodynamic Theory of Structure, Stability and Fluctuations, New York: Wiley-Interscience, 1971.
26. Ederer M, Gilles ED, Sawodny O. The Glansdorf–Prigogine stability criterion for biochemical reaction networks. *Automatica*. 2011;47: 1097–1104.

Appendix A: The Formal Structure of Thermodynamics

Callen[14] proposed the following postulates for an equilibrium system.

Postulate I. There exist particular states (called equilibrium states) that, macroscopically, are characterized completely by the specification of the internal energy U and a set of extensive parameters $X_1, \ldots, X_m$, later to be specifically enumerated.

Postulate II. There exists a function (called the entropy) of the extensive parameters, defined for all equilibrium states, and having the following property. The values assumed by the extensive parameters in the absence of a constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate III. The entropy of a composite system is additive over the constituent subsystems (whence the entropy of each constituent system is a homogeneous first-order function of the extensive parameters). The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

Postulate IV. The entropy vanishes in the state for which $T=(\partial U/\partial S)_{V,N_1\ldots,N_{n_c}}=0$.

We now derive the mathematical structure of equilibrium systems that closely mirrors the Callen postulates. Here, we follow Wightman[23] and Evans.[24] Let Z denote a point in an open convex subset $\mathbb{Z} \subset \mathbb{R}_+^{n_c+2}$ and let $S(Z)$ be a function defined on $\mathbb{Z}$. Postulates 2–4 are then written

Postulate II. $S : \mathbb{Z} \mapsto \mathbb{R}_+$ is concave

Postulate III. $S(\lambda Z)=\lambda S(Z)$ for any $\lambda > 0$ (the entropy is positively homogeneous degree one), $S \in \mathbb{C}_1$, and $T=\partial S/\partial U > 0$

Postulate IV. $S = 0$ whenever $T = 0$.

In our context, we define the vector Z so that

$$Z=(U, V, N_1 \ldots, N_{n_c})^T$$

It is worthwhile to explore the concavity property further as its relationship to the entropy maximization principle may not be evident at first sight. Imagine first that we have two systems A and B that are not in contact. These systems have states Z_A and Z_B and entropies $S(Z_A)$ and $S(Z_B)$. The overall entropy is

$$S=S(Z_A)+S(Z_B)$$

We now combine A and B to form a new system with state[†]

$$Z=Z_A+Z_B$$

The second law states that for any irreversible process, the entropy increases (Postulate II) until it reaches its maximum. Thus

$$S(Z_A+Z_B) \geq S(Z_A)+S(Z_B)$$

It follows that S is a concave function since for any $0 < \lambda < 1$

$$\begin{aligned} &S(\lambda Z_A+(1-\lambda)Z_B) \geq S(\lambda Z_A)+S((1-\lambda)Z_B) \\ &=\lambda S(Z_A)+(1-\lambda)S(Z_B) \end{aligned}$$

In second step, we used the homogeneous degree one property.

As S is $\mathbb{C}_1$ and monotone in U, we define

$$U=(S, V, N_1, \ldots, N_{n_c})$$

where U now is convex and $\mathbb{C}_1$. We can therefore, define the derivatives

$$T=\frac{\partial U}{\partial S}, \text{ Temperature}$$

$$P=-\frac{\partial U}{\partial V}, \text{ Pressure}$$

$$\mu_i=\frac{\partial U}{\partial N_i} \text{ Chemical potential, } i=1, \ldots, n_c$$

These variables can be viewed as force variables. At equilibrium differences among these vanish as seen in Definition 1. This principle can be reformulated as a minimization principle once we define the internal energy

$$dU=TdS-PdV+\sum_{j=1}^{n_c} \mu_j dN_j$$

From this perspective, the one-form TdS corresponds to infinitesimal heating and $PdV, \mu_j dN_j$ correspond to infinitesimal working. The equation above can be rearranged as

$$dS=\frac{1}{T}dU+\frac{P}{T}dV-\sum_{j=1}^{n_c}\frac{\mu_j}{T}dN_j$$

Due to homogeneity, we then have Definition 6

$$S=\frac{1}{T}U+\frac{P}{T}V-\sum_{j=1}^{n_C}\frac{\mu_j}{T}N_j$$

This equation, written on the form $S=S(U, V, N_1, \ldots., N_{n_c})$ is called the fundamental equation as it contains all thermodynamic information.

[†] *From physical point of view, we imagine that the new state is formed in a way that no work is done and no heat is transferred to or from the surrounding environment and that there are no chemical reactions. Sufficient time is then allowed to relax the system to achieve equilibrium.*

Theorem 4.

$$\delta Z^T M(Z)\delta Z=\delta^2 S(Z) \tag{A1}$$

Proof. The second variation of the entropy is given by

$$\begin{aligned}\delta^2 S&=\delta(\delta S)\\&=\delta\left(\frac{\partial S}{\partial Z}\delta Z\right)\\&=\delta w^T\delta Z+w^T\delta^2 Z\end{aligned}$$

The term $\delta^2 Z$ vanishes as a variation of a variation is equal to zero and we get

$$\delta^2 S=\delta Z^T\delta w \tag{A2}$$

From Eq. 8

$$\delta Z^T\delta w=\delta Z^T M\delta Z$$

and the result follows. □

The results above allow us to analyze the stability of perturbations along trajectories that are not necessarily defined *a priori*, using the second variation of the entropy as a Lyapunov function. This approach achieves global stability[22] and it is therefore considerably more general than the one proposed by Glansdorff and Prigogine (GP).[25] They defined the second variation relative to steady states by linearization. The GP type of analysis was recently applied for local stability analysis of some classes of chemical process systems by Ederer et al.[26]

Appendix B: The Entropy Balance

We consider the multicomponent flash system shown in Figure 3. The extension to a more general system with multiple inputs and outputs and more phases is straightforward and the result is provided at the end of the appendix. As is the case for all the systems we consider, we assume no chemical reactions, complete chemical, thermal, and hydrodynamic equilibrium between the vapor and liquid phases.

The balance Eq. 13 is repeated here for quick reference

$$\begin{aligned}\frac{dU}{dt}&=Fh_F-Dh_D-Lh_L+Q,\\\frac{dV_T}{dt}&=0\\\frac{dN_i}{dt}&=Fz_i-Dy_i-Lx_i\ \ i=1\ldots n_c\end{aligned} \tag{A4}$$

From the fundamental Eq. 6, we get

$$dS=\frac{1}{T}dU+\frac{P}{T}dV-\sum_{j=1}^{n_c}\frac{\mu_j}{T}dN_j$$

Assuming that the system evolves on the equilibrium manifold, we get

$$\frac{dS}{dt}=\frac{1}{T}\frac{dU}{dt}+\frac{P}{T}\frac{dV}{dt}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}\frac{dN_j}{dt}$$

Substituting the mass and energy balances in (A4) into this equation gives

$$\frac{dS}{dt}=\frac{1}{T}(Fh_F-Dh_D-Lh_L+Q)-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}(Fz_i-Dy_i-Lx_i)\right)$$

Rearranging terms according to the molar flow rates F, V, and L

$$\frac{dS}{dt}=F\left(\frac{h_F}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}z_j\right)-D\left(\frac{h_D}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}y_j\right)-L\left(\frac{h_L}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}x_j\right)+\frac{Q}{T} \tag{A5}$$

The molar entropies of vapor, liquid, and feed are given by

$$\begin{aligned}\hat{S}_F&=\frac{h_F}{T_F}-\sum_{j=1}^{n_c}\frac{\mu_{jF}}{T_F}z_j\\\hat{S}_D&=\frac{h_D}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}y_j\\\hat{S}_L&=\frac{h_L}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}x_j\end{aligned}$$

where T_F and μ_{jF} denote the feed temperature and component chemical potentials, respectively. Substituting these expressions into Eq. A5 gives

$$\frac{dS}{dt}=F\left(\frac{h_F}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}z_j\right)\pm F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}$$

To get the feed entropy flow in the balance, we have added and subtracted $F\hat{S}_F$. Hence

$$\frac{dS}{dt}=F\left(\frac{h_F}{T}-\sum_{j=1}^{n_c}\frac{\mu_j}{T}z_j\right)-F\left(\frac{h_F}{T_F}-\sum_{j=1}^{n_c}\frac{\mu_{jF}}{T_F}z_j\right)+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}$$

Rearranging to get the enthalpy h_{F} and feed composition z_{i} terms together

$$\frac{dS}{dt}=F\left(\frac{h_F}{T}-\frac{h_F}{T_F}-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}z_j-\frac{\mu_{jF}}{T_F}z_j\right)\right)+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}$$

Replacing h_F with $\hat{U}_F+P_F\hat{V}_F$, where $\hat{U}_F$ is the molar internal energy, P_F pressure, and $\hat{V}_F$ the molar volume of feed and gathering terms gives

$$\begin{aligned}\frac{dS}{dt}=&F\left(\left(\frac{1}{T}-\frac{1}{T_F}\right)\hat{U}_F+\left(\frac{P_F}{T}-\frac{P_F}{T_F}\right)\hat{V}_F-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}z_j-\frac{\mu_{jF}}{T_F}z_j\right)\right)\\&+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}\end{aligned}$$

We add and subtract P/T within terms multiplied with $\hat{V}_F$ to give

$$\begin{aligned}\frac{dS}{dt}=&F\left(\left(\frac{1}{T}-\frac{1}{T_F}\right)\hat{U}_F+\left(\frac{P_F}{T}-\frac{P}{T}+\frac{P}{T}-\frac{P_F}{T_F}\right)\hat{V}_F-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}z_j-\frac{\mu_{jF}}{T_F}z_j\right)\right)\\&+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}\end{aligned}$$

Rearranging again gives

$$\frac{dS}{dt}=F\left(\left(\frac{1}{T}-\frac{1}{T_F}\right)\hat{U}_F+\left(\frac{P}{T}-\frac{P_F}{T_F}\right)\hat{V}_F-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}z_j-\frac{\mu_{jF}}{T_F}z_j\right)\right)$$
$$+F\left(\frac{P_F}{T}-\frac{P}{T}\right)\hat{V}_F+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}$$

We now define the temperature scaled availability so that

$$\hat{A}_F=\left(\frac{1}{T}-\frac{1}{T_F}\right)\hat{U}_F+\left(\frac{P}{T}-\frac{P_F}{T_F}\right)\hat{V}_F-\sum_{j=1}^{n_c}\left(\frac{\mu_j}{T}-\frac{\mu_{jF}}{T_F}\right)z_j$$

The availability denotes the work per unit mole done by the feed by equilibrating against the flash. Using this notation, we have

$$\frac{dS}{dt}=F\hat{A}_F+F\left(\frac{P_F}{T}-\frac{P}{T}\right)\hat{V}_F+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T}$$

Let T_0 denote the temperature at which heat is supplied from the environment. Adding and subtracting Q/T_0 then gives

$$\frac{dS}{dt}=F\hat{A}_F+F\left(\frac{P_F}{T}-\frac{P}{T}\right)\hat{V}_F+\left(\frac{1}{T}-\frac{P}{T_0}\right)Q+F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T_0}$$

Thus, we get

$$\frac{dS}{dt}=F\hat{S}_F-D\hat{S}_D-L\hat{S}_L+\frac{Q}{T_0}+F\hat{A}_F+F\frac{\hat{V}}{T}(P_F-P)+Q\left(\frac{1}{T}-\frac{1}{T_0}\right) \tag{A6}$$

We now introduce the notation $S_F=F\hat{S}_F, S_D=D\hat{S}_D$, $S_L=L\hat{S}_L$ to denote the entropy flow and $F_A=F\hat{A}_F$ rate of irreversible loss of available work due to sudden change of conditions as the fluid expands into the flash from a high to a low pressure. Equation A6 can then be written[14,20]

$$\frac{dS}{dt}=\underbrace{S_F-S_D-S+\frac{Q}{T_0}}_{\text{Entropy flux - }\phi_S}+\underbrace{A_F+F\frac{\hat{V}}{T}(P_F-P)+Q\left(\frac{1}{T}-\frac{1}{T_0}\right)}_{\text{Entropy Production - }\sigma_S} \tag{A7}$$

The main reason for writing the equation this way is to highlight the fact that the entropy balance is written in terms of entropy and availability fluxes that are, respectively, concave and convex in terms of the flow vectors.

The balance for an equilibrium system with n inlet flows with rates F_i and m outlet flows with rates D_i, which may be liquid or vapor, are developed along the same lines as for the multicomponent flash. We get

$$\frac{dS}{dt}=\underbrace{\sum_{i=1}^{n}F_i\hat{S}_{Fi}-\sum_{i=1}^{m}D_i\hat{S}_{Di}+\frac{Q}{T_0}}_{\text{Entropy flux - }\phi_S}$$
$$+\underbrace{\sum_{i=1}^{n}F_i\left(\hat{A}_i+\frac{\hat{V}_i}{T}(P_i-P)\right)+Q\left(\frac{1}{T}-\frac{1}{T_0}\right)}_{\text{Entropy Production - }\sigma_S} \tag{A8}$$

Manuscript received Feb. 10, 2013, and revision received July 15, 2013.