Thermodynamic Approach to the Structural Stability of Process Plants

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A thermodynamic approach for analyzing the structural stability of process plants is presented. The results are connected with a theory of systems described by dynamic conservation balances using a potential for stability analysis that generalizes the availability/exergy. This theory is used to show that interconnected systems with no source terms and Kirchhoff convection are structurally asymptotically stable. The approach is applicable for systems where only Kirchhoff convective transport and transfer processes with equilibrium take place. Systems with constant mass holdup in every balancing volume satisfy the condition of Kirchhoff convection. The general results are illustrated in examples of practical importance including heat exchanger networks, multicomponent flash, and multicomponent distillation with constant molar flows.

Introduction

Stability analysis of process systems plays an important role not only in analysis and design of their operating conditions but also in process control. The topic has received considerable attention in process engineering from both a design and control perspective, as pointed out by Hangos and Perkins (1997). Recently, interests moved into the combined area of design/control integration (Perkins and Walsh, 1996). Today, it is well accepted that economically optimal process plants can be difficult, or even impossible, to operate safely. As a consequence, efforts are directed to systematic approaches to address both unit interconnections and dynamic operation during the early stages of the design project (see, for instance, the works by Luyben and Floudas, 1994a,b, or Barhi et al., 1997). The problem is treated in an optimization framework through the notion of backoff (Perkins and Walsh, 1996). In this way, the dynamic effect of a family of possible plant disturbances is included in the optimization problem that, in conjuction with the optimal unit interconnection, selects the appropriate input−output pairings and controller configurations.

In this article, the stability analysis of process systems is based on the theory of passive systems (Desoer and Vidyasagar, 1975). Passivity theory plays a key role in analyzing the stability of nonlinear systems; it is shown that passive systems are asymptotically stable under mild conditions (Hill and Moylan, 1980). A dynamic system is called passive if it is equipped with a real function $\mathfrak{F}$ related to the input−output set (u, y), satisfying the following inequality:

$$\mathfrak{F}(t+\tau) - \mathfrak{F}(t) \leq \int_t^{t+\tau} u^T y \, dt \tag{1}$$

for any $\tau > 0$. $\mathfrak{F}$ is a bounded function ($\mathfrak{F} > 0$), referred to as the *storage*, and accounts for the total generalized energy stored in the system. Inequality 1 simply states that for a pas-

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sive system, the amount of energy stored at any time interval can never be larger than that supplied from the environment. In this way, the inequality acts as a constraint that restricts the evolution of the system while it relates states (associated with the storage) to inputs and outputs, which are implicit in the supply term.

This particular representation of the supply suggests control laws $u(y)$ with the property $u^T(y)y \leq 0$ so that $\mathfrak{F}$ remains bounded, which in turn guarantees that the states of the system converge to a bounded set called *passive set*, that is, asymptotically stable. From a control design perspective, the interesting property of passive systems is that their passive interconnection is also passive. Thus, structurally stable plants will remain stable for any control structure satisfying the constraint expressed in Eq. 1.

It is worth noting that this passivity formalism generalizes Lyapunov theory in the sense that $\mathfrak{F}$ does not need to be known explicitly (Slotine and Li, 1991). In fact, the only condition that it should satisfy is that of being lower bounded. The price to pay is that further conditions need be imposed on the system in order to determine the type of convergence. In addition, it is usually quite difficult to identify constraints of the form of Eq. 1 for a general class of systems such as process systems.

In our analysis we use a novel approach (Ydstie and Alonso, 1997) that is based on thermodynamics and integrates process systems into the formalism of passivity theory. Some other results on convective transport matrices (Hangos and Perkins, 1997) are also used to resolve structural stability for a broad class of process plants.

The outline of the article is as follows. In the following section the basic assumptions and the general form of the dynamic models are formulated, along with the necessary thermodynamic background. In this section, the basic ingredients of our analysis are also briefly described, namely, the formulation of the convective interconnections through Kirchhoff convection matrices, the thermodynamic representation of transfer rate expressions, and the fundamentals of passivity formalism in a thermodynamic context.

The main stability results for general process plant interconnections without source terms are then presented. Finally, these results are illustrated by examples of practical importance: heat exchanger networks, multicomponent flash, and multicomponent distillation with constant molar flows.

Basic Assumptions and Tools

Dynamic system models applied to process control differ substantially from models used in other control fields, such as mechanical and transport. Their speciality is explained by the fact that the dynamic models of process systems usually stem from dynamic conservation balances for extensive conserved quantities coupled with suitable algebraic constitutive equations of mixed origin (Hangos and Cameron, 1997; Ydstie and Alonso, 1977; Farschman et al., 1998). Some of the constitutive equations describe thermodynamical relations such as state equations and thermodynamical property relations.

In this section we describe the class of systems under study as well as some important tools and properties connected with their structural stability.

Modeling assumptions for a class of dynamic process models

Process plants can be described by lumped cascade models for the purpose of their dynamic analysis, control, and diagnosis. This results in a lumped parameter model of a process plant suitable for analysis. We restrict ourselves to process plants for which the following assumptions hold:

1. The model of the operating units are approximated by cascade models, that is, by networks of regions. A region j ($j = 1, \ldots, \mathfrak{C}$) can be regarded as an elementary balancing volume for which lumped dynamic conservation balances are set up. Therefore either one perfectly stirred phase or multiple phases in physical equilibrium are present in a region. *The regions are the elementary dynamic units of the whole processing plant model.*

2. No dynamic effect (for example, delay) caused by connections between regions (e.g., piping between operating units) is taken into account.

3. The submodels of the regions are constructed from first engineering principles, that is, from dynamic balance equations for conserved extensive quantities ($\phi^{(j)}$), which are

- Component masses ($m_k^{(j)}$, $k = 1, \ldots, \mathcal{K}$), with $m_{\mathcal{K}+1}^{(j)}$ being the total mass, that is, $m_{\mathcal{K}+1}^{(j)} = \sum_{k=1}^{\mathcal{K}} m_k^{(j)}$;
- Internal energy ($E^{(j)}$).

This assumption is formalized in mathematical terms by defining a vector of intensive variables:

$$\pi^{(j)} \in \Pi^{(j)} = \left[e^{(j)}, c_k^{(j)}, k = 1, \ldots, \mathcal{K}+1 \right]^T, \qquad (2)$$

where $e^{(j)}$, $c_k^{(j)}$ represent the volume-specific internal energy and concentrations of component k, respectively, in the region j. The relationship between volume-specific intensive and extensive properties is as follows:

$$\phi^{(j)} = H^{(j)} \pi^{(j)} + \phi_{ref}^{(j)}, \qquad (3)$$

where $H^{(j)}$ is the volume (holdup) of region j, and $\phi_{ref}^{(j)}$ is an arbitrary reference.

4. Constant holdup is assumed in each region, that is,

$$H^{(j)} = \text{const.} \qquad (4)$$

5. Constant molar flow rates are assumed for all convective flows.

The two preceding assumptions are used mainly for technical reasons. With a constant holdup $H^{(j)}$ in region j a simple relation can be established between the extensive conserved quantities $\phi^{(j)}$ and their *intensive potential counterpart* $\varphi^{(j)}$, which acts as a driving force for the transfer of the extensive quantity (temperature for energy, composition for component mass) in the form of

$$\phi^{(j)} = C_\varphi H^{(j)} \varphi^{(j)} + \phi_{ref}^{(j)}, \qquad (5)$$

where

$$\varphi^{(j)} \in \mathfrak{X}^{(j)} = \left[T^{(j)}, c_k^{(j)}, k = 1, \ldots, \mathcal{K}+1 \right]^T \qquad (6)$$

$C_\varphi = 1$ or $C_\varphi = c_P$, and $\phi^{(j)}_{ref}$ represents an arbitrary reference.

6. All phases involved are assumed to be incompressible by constant pressure. Moreover the temperature, pressure, and composition dependence of their physical properties, such as density (ϱ) and specific heat (c_P), are assumed to be negligible.

As a consequence of the preceding assumptions, *no balance equation is needed for the overall mass in any region.* For the purposes of the thermodynamic analysis to be developed in this article, we add the following assumption:

7. Local thermodynamical equilibrium is assumed everywhere in each region j. This assumption is standard in the theory of irreversible thermodynamics, and the range of validity covers most of the operating conditions met in practice [e.g., see Glansdorff and Prigogine (1974) or Kreuzer (1983)]. It simply states the validity of the Gibbs−Duhem relationship for open systems that are out of equilibrium, of the form:

$$S^{(j)} = A^{T(j)}\Phi^{(j)} + \left(\frac{P}{T}\right)^{(j)} H^{(j)}, \tag{7}$$

where

$$A^{(j)} = \left[\left(\frac{1}{T}\right)^{(j)}, \quad \left(\frac{\mu_k}{T}\right)^{(j)}, \quad k = 1, \ldots, \mathfrak{K}\right]^T. \tag{8}$$

The vector $A^{(j)}$ stands for the corresponding intensive (potential) properties of the conserved extensive quantities in $\Phi^{(j)}$

$$\Phi^{(j)} = \left[E^{(j)}, m_k^{(j)}, k = 1, \ldots, \mathfrak{K}\right]^T. \tag{9}$$

Process systems

According to the definition given by Ydstie and Alonso (1997), *process systems* are those that support the laws of thermodynamics. The first law provides conservation of mass and energy, which are the basic ingredients for process modeling. They are complemented by modeling assumptions and constitutive relations in the form of algebraic equations. This subsection is devoted to the general form of these principles and their consequences.

Conservation Balances. The lumped dynamic balance equations satisfying the basic assumptions for the volume-specific extensive variables $\pi^{(j)} \in \Pi^{(j)}$ in the region j are in the following general form:

$$\frac{dH^{(j)}\pi^{(j)}}{dt} = F^{(j)}_{\pi\,\mathrm{in}} - F^{(j)}_{\pi\,\mathrm{out}} + \sum_{k \neq j} \psi^{(jk)}_{\pi t} + \psi^{(j)}_{\pi s}, \tag{10}$$

where $H^{(j)}$ represents holdup; $\psi^{(jk)}_{\pi t}$ is the rate of property transferred between regions j and k; $\psi^{(j)}_{\pi s}$ is a source or production term mainly associated with chemical reactions; and $F^{(j)}_\pi$ represents the input and output convection flux for the property $\pi^{(j)}$. Denoting the output flow rate of region j by $\upsilon^{(j)}$, the output convection term takes the form

$$F^{(j)}_{\pi\,\mathrm{out}} = \upsilon^{(j)}\pi^{(j)}. \tag{11}$$

Entropy Balance. The second law states the existence of an extensive property called entropy that satisfies the following conservation-like principle:

$$\frac{dS^{(j)}}{dt} = F_s^{(j)} + P_s^{(j)}, \tag{12}$$

where $S^{(j)}$ is the amount of entropy accumulated in region j; and $F_s^{(j)}$ and $P_s^{(j)}$ are the net flux through the boundary of j and the rate of entropy produced in j, respectively. The particularity of Eq. 12 is in the production term, which according to the second law is of the form $P_s^{(j)} \geq 0$ with equality at equilibrium. For a detailed discussion of the idea of a process systems, see Ydstie and Alonso (1997). The assumption of local equilibrium ensures that $S^{(j)}$ is a *first-order homogeneous* function of the extensive properties, while its density ($s^{(j)}$) is a concave function with respect to the properties $\pi^{(j)}$.

Concavity of entropy density implies that its Hessian with respect to $\pi^{(j)}$ is negative definite. It is expressed as a matrix M with elements

$$M_{k\ell} = \frac{\partial^2 s^{(j)}}{\partial \pi_k^{(j)} \partial \pi_\ell}^{(j)} < 0 \qquad k, \ \ell = 1, \ldots, \mathfrak{K} + 1. \tag{13}$$

Equation 13 preserves the one-to-one mapping between vectors π and A. From homogeneity, Eq. 7 can be written in differential form as follows:

$$dS^{(j)} = \left(\frac{1}{T}\right)^{(j)} dE^{(j)} + \left(\frac{P}{T}\right)^{(j)} dV^{(j)} - \sum_{k=1}^{\mathfrak{K}} \left(\frac{\mu_k}{T}\right)^{(j)} dN^{(j)}, \tag{14}$$

where the operator d stands for total derivative. Since $H^{(j)}$ is constant, that is, $dV^{(j)} = 0$, the explicit form of the Hessian (Eq. 13) is obtained by applying the total derivative d to Eq. 14, resulting in the following matrix:

$$M = \begin{bmatrix} -1/C_\upsilon T^2 & 0 & \cdots & 0 \\ 0 & -\mu_{11}/T & \cdots & -\mu_{1\mathfrak{K}}/T \\ 0 & \cdots & \cdots & \cdots \\ 0 & -\mu_{\mathfrak{K}1}/T & \cdots & -\mu_{\mathfrak{K}\mathfrak{K}}/T \end{bmatrix}, \tag{15}$$

where

$$C_\upsilon = \left(\frac{\partial e}{\partial T}\right)_{c_j} \qquad \mu_{jk} = \left(\frac{\partial \mu_j}{\partial c_k}\right)_{T, c_i}.$$

The matrix, M, as was said before, is negative definite. Combining Eqs. 14 and 10 and using t as a parameter, an equation of the form of Eq. 12 is obtained, with

$$F_s^{(j)} = \left(\sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} F_{\pi_i}^{(j)} \right)_{\text{in}} - \left(\sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} F_{\pi_i}^{(j)} \right)_{\text{out}} + \left(\sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \sum_{j \neq k} \psi_{\pi_{it}}^{(jk)} \right) \tag{16}$$

$$P_s^{(j)} = \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \psi_{\pi_{is}}^{(j)}. \tag{17}$$

It is worth noting that perfect mixing implies that entropy in the region is produced exclusively from sources such as chemical reactions. However, when different regions (phases) are in contact, a new source of entropy production due to transfer by driving forces appears. To show this, we first note that for a composite system consisting of $\mathfrak{C}$ regions that all touch each other, the total entropy is calculated as

$$S = \sum_{j=i}^{\mathfrak{C}} S^{(j)} = \sum_{j=i}^{\mathfrak{C}} H^{(j)} s^{(j)}. \tag{18}$$

Let us consider a composite system composed of two regions j and k with transfer between them. The dynamic model for each region becomes:

$$\frac{dH^{(j)}\pi_i^{(j)}}{dt} = F_{\pi,\text{in}}^{(j)} - \upsilon^{(j)}\pi_i^{(j)} + \psi_{\pi_i t}^{(jk)} + \psi_{\pi_i s}^{(j)}$$

$$\frac{dH^{(k)}\pi_i^{(k)}}{dt} = F_{\pi,\text{in}}^{(k)} - \upsilon^{(k)}\pi_i^{(k)} + \psi_{\pi_i t}^{(kj)} + \psi_{\pi_i s}^{(k)}.$$

To obtain the total entropy we use Eq. 18 with $s^{(j)} = \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \pi_{\mathrm{i}}^{(j)}$. Following the same steps as in the derivation of Eqs. 16 and 17, we obtain for each region:

$$\frac{dH^{(j)}s^{(j)}}{dt} = \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} F_{\pi_i}^{(j)} - \sum_{i=1}^{\mathfrak{K}+2} \upsilon^{(j)} A_i^{(j)} \pi_i^{(j)} + \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \psi_{\pi_i t}^{(jk)} + \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \psi_{\pi_i s}^{(j)} \tag{19}$$

Using Eqs. 18 and 19, a new term of the form appears:

$$P_s' = \sum_{i=1}^{\mathfrak{K}+2} \left(A_i^{(j)} - A_i^{(k)} \right) \psi_{\pi_i t}^{(jk)}, \tag{20}$$

which, since transfer always occurs in the direction of the positive driving forces, is positive definite. This constraint should be respected when formulating the driving forces in transfer terms.

Entropy production then becomes

$$P_s^{(j)} = \sum_j \sum_{i=1}^{\mathfrak{K}+2} A_i^{(j)} \psi_{\pi_i s}^{(j)} + \sum_{j \neq k} \sum_{i=1}^{\mathfrak{K}+2} \left(A_i^{(j)} - A_i^{(k)} \right) \psi_{\pi_i t}^{(jk)}.$$

Positive definiteness in P_s' follows through the so-called Onsager relations (Kreuzer, 1983), which establish links between the driving forces and the transfer rates of the form:

$$\psi_{\pi_i t}^{(jk)} = \sum_{m=1}^{\mathfrak{K}+1} \ell_{im}^{jk} \left(A_m^{(j)} - A_m^{(k)} \right),$$

with ℓ_{im}^{jk} being the i,m element of a positive definite and a symmetric matrix of transport coefficients $L > 0$. This way the entropy balance connects the other balances constituting process engineering models and sets up an additional constraint that can be used for stability analysis. This constraint will be described in more detail in the subsection on stability analysis of process systems via passivity theory.

Convective transport, connections

In the case of connections representing convective transport between regions, the single-region input convective transport term

$$F_{\pi_i\text{in}}^{(j)} = \upsilon^{(j)} \pi_{iB}^{(j)}$$

with π_{iB} being the inlet value of the quantity, is replaced by

$$F_{\pi_i\text{in}}^{(j)} = \upsilon^{(j)} \left(\sum_{\ell=1}^{\mathfrak{C}} \left[\alpha_\ell^{(j)} \pi_i^{(\ell)} \right] + \alpha_0^{(j)} \pi_{iB}^{(j)} \right), \tag{21}$$

with

$$\sum_{\ell=0}^{\mathfrak{C}} \alpha_\ell^{(j)} = 1, \tag{22}$$

where the input of the jth region is connected to the mixed stream from the outputs of the other regions and from an external input stream $\pi_{iB}^{(j)}$. Note that the new input convective term (Eqs. 21 and 22) is a convex linear combination of the output convective terms of all the regions including the jth one, that is, the factors in the linear combination in Eq. 21 fulfill Eq. 22.

It is important to note here that the convexity property given earlier is a consequence of the constant molar flow, constant holdup, and constant physical properties assumptions in the Basic Assumption and Tools section.

Kirchhoff Convection Matrices. The constant holdup assumption for every region of the overall process system implies properties of the convection network that will be important later for the structural stability analysis. In order to show this, let us represent the environment of the process system by a virtual region of region index $j = 0$. The situation is shown in Figure 1.

Because constant holdup is assumed in every region, the sum of convective inflows

$$\upsilon^{(0)} = \sum_{\ell=1}^{\mathfrak{C}} \alpha_0^{(\ell)} \upsilon^{(\ell)} \tag{23}$$

is equal to the sum of the convective outflows of the process system. It is important to note that the composite system,

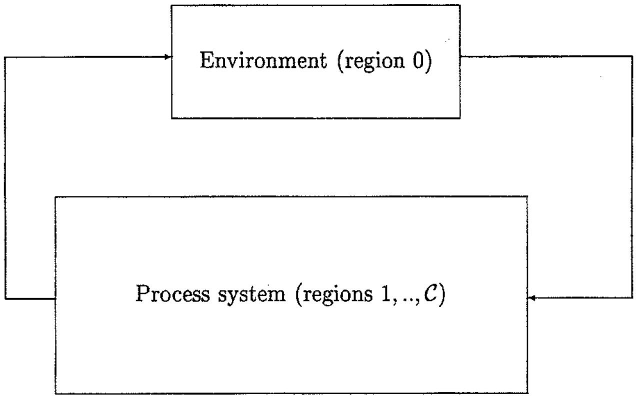

Figure 1. Kirchhoff convection.

consisting of the original process system and its environment, is closed with $\mathfrak{C}+1$ regions, each of constant holdup.

The convective outflow from region j is subdivided between the other regions and the environment, giving

$$v^{(j)}=\sum_{\ell=0}^{\mathfrak{C}}\alpha_j^{(\ell)}v^{(\ell)},\qquad j=0,\ldots,\mathfrak{C}.\tag{24}$$

The notation of the convective flow around a region is shown in Figure 2.

We can use this notation to formulate the mass balances for every region, taking into account that the physical properties such as density are constant:

$$\begin{bmatrix}\dfrac{dH^{(0)}}{dt}\\ \dfrac{dH^{(1)}}{dt}\\ \cdots\\ \dfrac{dH^{(\mathfrak{C})}}{dt}\end{bmatrix}=\begin{bmatrix}-\left(1-\alpha_0^{(0)}\right)v^{(0)} & \alpha_0^{(1)}v^{(1)} & \alpha_0^{(2)}v^{(2)} & \cdots & \alpha_0^{(\mathfrak{C})}v^{(\mathfrak{C})}\\ \alpha_1^{(0)}v^{(0)} & -\left(1-\alpha_1^{(1)}\right)v^{(1)} & \alpha_1^{(2)}v^{(2)} & \cdots & \alpha_1^{(\mathfrak{C})}v^{(\mathfrak{C})}\\ \cdots & & & & \\ \alpha_{\mathfrak{C}}^{(0)}v^{(0)} & \alpha_{\mathfrak{C}}^{(1)}v^{(1)} & \alpha_{\mathfrak{C}}^{(2)}v^{(2)} & \cdots & -\left(1-\alpha_{\mathfrak{C}}^{(\mathfrak{C})}\right)v^{(\mathfrak{C})}\end{bmatrix}\begin{bmatrix}1\\ 1\\ \cdots\\ 1\end{bmatrix},\tag{25}$$

where the coefficient matrix on the righthand side will be denoted by $C_{\mathfrak{C}}$ and termed Kirchhoff convection matrix (see the Appendix). The constant holdup assumption implies that

$$C_{\mathfrak{C}}\begin{bmatrix}1\\ 1\\ \cdots\\ 1\end{bmatrix}=\begin{bmatrix}0\\ 0\\ \cdots\\ 0\end{bmatrix},\tag{26}$$

which is also a consequence of Eq. 22.

Moreover, Eq. 24 implies that

$$[1\quad 1\quad \cdots\quad 1]C_{\mathfrak{C}}=\begin{bmatrix}0\\ 0\\ \cdots\\ 0\end{bmatrix}.\tag{27}$$

The two preceding equations and the sign pattern of $C_{\mathfrak{C}}$ show that Kirchhoff convection matrices are both row and column conservation matrices. Moreover, it can be shown (see the subsection in the Appendix on properties of Kirchoff convection matrices) that Kirchhoff convection matrices are negative semidefinite matrices, that is, $C_{\mathfrak{C}}\leq 0$.

Transfer-rate expressions

When several phases are in mutual contact, the second law of thermodynamics imposes a transfer of the extensive thermodynamic properties π in the direction of the gradients associated with the vector of intensive variables A. In the light of assumption 1 (complete mixing in each region), the trans-

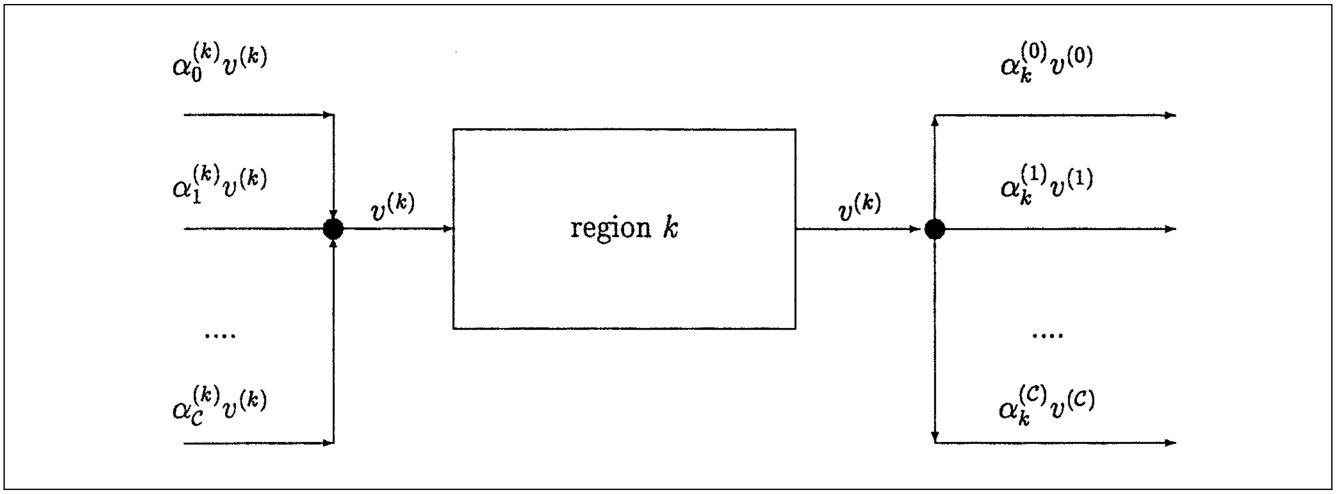

Figure 2. Convective environment of a region.

fer rate becomes a function of the difference in the potential vector among these phases. We refer to that difference as the driving-force vector, which is of the form:

$$\tilde{A} = A^{(j)} - A^{(k)}.$$

It is important to note here that the intensive variables in the two regions are equal in equilibrium, that is, $A^{*(j)} = A^{*(k)}$. Therefore the driving force vector can be written as

$$\tilde{A} = A^{(j)} - A^{(k)} = \overline{A}^{(j)} - \overline{A}^{(k)}, \tag{28}$$

where

$$\overline{A}^{(j)} = A^{(j)} - A^{*(j)}, \qquad \overline{A}^{(k)} = A^{(k)} - A^{*(k)}$$

are the deviations from the equilibrium values.

When operating near equilibrium, the so-called linear branch (Glansdorff and Prigogine, 1971) of irreversible thermodynamics provides an explicit relationship between the driving forces and the thermodynamic fluxes (transfer rates), known as Onsager relations, which can be written as

$$J = L\tilde{A}, \qquad L = L^T, \qquad L > 0, \tag{29}$$

where L is a symmetric and positive definite matrix of transport coefficients (Kreuzer, 1983). The matrix will not generally be in a diagonal form, thus accounting for the coupled contributions of the driving forces to a particular transfer rate. It should be noted that multiphase transport processes are usually decomposed into transport processes between pairs of phases by assuming additivity of the transport phenomena.

The preceding thermodynamic description provides a general framework upon which the traditional transfer-rate representations for engineering models can be based. Although the engineering expressions are simplified versions of the structure given by Eq. 29, their parameters and variables are more easily identified by an experiment, and therefore are more appropriate for modeling purposes. The two most traditional ways of expressing the transfer term $\Psi_{\pi t}^{(j)}$ in Eq. 10 are briefly described next and are related to the thermodynamic description presented earlier.

Difference-Based Driving Force. In the first case, it is assumed that transfer rate depends on the difference between the intensive variables $\varphi^{(j)}$ and $\varphi^{(\ell)}$ (see Eq. 6) in the jth and ℓth regions:

$$\Psi_{\pi t}^{(j)} = \sum_{\ell=1}^{\mathfrak{e}} \psi_{\pi t}^{(j\ell)} = \sum_{\ell=1}^{\mathfrak{e}} K_{\pi t}^{(j\ell)}\left(\varphi^{(\ell)} - \varphi^{(j)}\right). \tag{30}$$

Note that, for the transfer coefficients, a positive constraint holds:

$$K_{\pi t}^{(j\ell)} > 0, \tag{31}$$

if the particular transfer term

$$\psi_{\pi t}^{(j\ell)} = K_{\pi t}^{(j\ell)}\left(\varphi^{(\ell)} - \varphi^{(j)}\right)$$

is directed from the ℓth region into the jth region in the direction of the positive driving forces. Moreover, as a consequence of Eqs. 3 and 5, under our basic assumptions the simple relation

$$\pi^{(j)} = C_\varphi \varphi^{(j)}, \qquad C_\varphi > 0 \tag{32}$$

holds between the potential and the volume-specific extensive variables. With this, Eq. 30 takes the following form:

$$\Psi_{\pi t}^{(j)} = \sum_{\ell=1}^{\mathfrak{e}} \psi_{\pi t}^{(j\ell)} = \sum_{\ell=1}^{\mathfrak{e}} \frac{K_{\pi t}^{(j\ell)}}{C_\varphi}\left(\pi^{(\ell)} - \pi^{(j)}\right). \tag{33}$$

Here, the positive constraint is a consequence of the second law of thermodynamics (see Eq. 20) and could be used to prove stability for the class of process systems.

However, our analysis is based on the more general relation, Eq. 29. In this context, it should be noted that variables defined in Eqs. 6 and 8, although both intensive in nature, are related by nonlinear mappings and therefore cannot be directly interchanged in Eq. 30.

Equilibrium Value-Based Driving Force. The other way of describing the transfer rate is by defining the driving forces for each region as the difference between the actual $\varphi^{(j)}$ and equilibrium value $\varphi^{*(j)}$ of the potential. This leads to a transfer rate defined as

$$\Psi_{\pi t}^{(j)} = \sum_{\ell=1}^{\mathfrak{e}} k_{\pi t}^{(j\ell)}\left(\varphi^{*(j)} - \varphi^{(j)}\right) = \sum_{\ell=1}^{\mathfrak{e}} \frac{k_{\pi t}^{(j\ell)}}{C_\varphi}\left(\pi^{*(j)} - \pi^{(j)}\right). \tag{34}$$

The nonlinear equilibrium relationship provides a constraint for the equilibrium values. This ensures that the partial transfer rates of the same quantity between regions j and ℓ are expressed in two different, although equivalent, ways

$$\psi_{\pi t}^{(j\ell)} = \frac{k_{\pi t}^{(j\ell)}}{C_\varphi}\left(\pi^{*(j)} - \pi^{(j)}\right) = \frac{k_{\pi t}^{(j\ell)}}{C_\varphi}\left(\pi^{*(\ell)} - \pi^{(\ell)}\right). \tag{35}$$

These expressions provide good approximations of the real transfer rates when the stationary point around which the system operates is close to equilibrium.

Relation Between the Engineering and Thermodynamical Description. First, we observe that the equilibrium value-based form of the transfer rate in Eq. 35 does not differ substantially from the difference-based form when the equivalent forms of the driving force in Eq. 28 are considered.

As we show next, Eq. 30 can be seen as a linearized version of Eq. 29. Let us consider the energy flux $J_E^{(j\ell)}$ with its associated driving force:

$$\tilde{A}_E^{(j\ell)} = \left(\frac{1}{T^{(j)}} - \frac{1}{T^{*(j)}}\right) - \left(\frac{1}{T^{(\ell)}} - \frac{1}{T^{*(\ell)}}\right) = \frac{\overline{1}}{T^{(j)}} - \frac{\overline{1}}{T^{(\ell)}}. \tag{36}$$

For the component mass flux $J_{m_k}^{(j\ell)}$, the corresponding driving force is

$$\tilde{A}_{m_k}^{(j\ell)} = \frac{\overline{\mu_k^{(j)}}}{T^{(j)}} - \frac{\overline{\mu_k^{(\ell)}}}{T^{(\ell)}}. \tag{37}$$

It is important to note that in most practical cases the cross-effect between mass and energy fluxes is neglected, so we have $L_{Em_k} = 0$.

In order to obtain these fluxes in the conventional process-engineering form, the dependence of the chemical potential on the temperature and concentrations should be considered. This is of the form:

$$\mu_k^{(\ell)} = \mu_{k\ell}^0 + RT^{(\ell)} \ln\left(\gamma_k^{(\ell)} c_k^{(\ell)}\right) \tag{38}$$

for liquid phases, with $\gamma_k^{(\ell)}$ being the activity coefficient, and

$$\mu_k^{(j)} = \mu_{kj}^0 + RT^{(j)} \ln\left(f_k^{(j)} c_k^{(j)}\right) \tag{39}$$

for vapor phases, with $f_k^{(j)}$ being the fugacity coefficient. Note that for *ideal mixtures* in both regions the activity and fugacity coefficients are constant and equal to 1.

In equilibrium, $\mu_k^{(\ell)} = \mu_k^{(j)}$ holds for every $k = 1, \ldots, \mathcal{K}$ and $T^{(\ell)} = T^{(j)} = T^*$, which gives the following algebraic relationships between the equilibrium concentrations

$$\frac{c_k^{*(j)}}{c_k^{*(\ell)}} = \frac{\gamma_k^{(\ell)}}{f_k^{(j)}} e^{(\mu_{k\ell}^0 - \mu_{kj}^0)/RT^*}. \tag{40}$$

First-order linearization of Eqs. 36 and 37 around the equilibrium point $\varphi^{*(j)} = [T^{*(j)}, c_k^{(j)}, k = 1, \ldots, \mathcal{K}]^T$ for $j = 1, \ldots, \mathfrak{C}$, leads to the following expression, valid for each phase:

$$A = A^* + \left(\frac{\partial A}{\partial \pi}\right)_{\pi^*} \left(\frac{\partial \pi}{\partial \varphi}\right)_{\varphi^*} (\varphi - \varphi^*), \tag{41}$$

where, as pointed out in the subsection on process systems,

$$\left(\frac{\partial A}{\partial \pi}\right)_{\pi^*} = M = \frac{\partial^2 s}{\partial \pi_k \partial \pi_\ell}, \tag{42}$$

since the holdup $H^{(j)}$ is constant. The term $(\partial\pi/\partial\varphi)_{\varphi^*}$ consists of a diagonal matrix, with all the elements but the first one, which is C_v, being unity, and consequently:

$$M' = M\left(\frac{\partial \pi}{\partial \varphi}\right)_{\varphi^*}$$

is also a symmetric and negative definite matrix determined at equilibrium. Linearized fluxes (Eq. 29) then become

$$J^{(j,\ell)} = \overline{L}^{(j,\ell)} \overline{D}^{(j,\ell)}, \tag{43}$$

with

$$\overline{D}^{(j,\ell)} = \begin{bmatrix} \overline{T}^{(\ell)} - \overline{T}^{(j)} \\ \overline{c}_1^{(\ell)} - \overline{c}_1^{(j)} \\ \cdots \\ \overline{c}_{\mathcal{K}}^{(\ell)} - \overline{c}_{\mathcal{K}}^{(j)} \end{bmatrix} \tag{44}$$

and $\overline{L}^{(j,\ell)} = LM'$. This matrix is still *symmetric*, but the off-diagonal elements $\overline{L}_{Tc_k}$ will not be zero anymore. Positive definiteness of $\overline{L}$ cannot be, in the general case, guaranteed either.

Stability analysis of process systems via passivity theory

In this section we look into the definitions and properties of process systems given earlier to develop inequalities of the form of Eq. 1. However, entropy is not bounded and therefore cannot be used as a storage function. This can be accomplished by constructing exergylike functions, as described below. A detailed version of the theoretical aspects is presented in Ydstie and Alonso (1997). We review the main results and give some generalizations below. These results follow directly from the concavity of the entropy function.

To illustrate the application of passivity theory and show structural stability, let us consider a particular process configuration. This configuration consists of a number of phases or regions $\mathfrak{C}$ in mutual contact, each of which has an input and output convective flow so the convective matrix takes the form:

$$C_{\mathfrak{C}} = \begin{bmatrix} -v^{(1)} & 0 & \cdots & 0 \\ 0 & -v^{(2)} & \cdots & 0 \\ \cdots & 0 & -v^{(j)} & \cdots \\ 0 & \cdots & \cdots & -v^{(\mathfrak{C})} \end{bmatrix}. \tag{45}$$

The preceding convective matrix describes the situation when no convective connection exists between the regions, each region having its own convective inflow and outflow to the environment.

A reference state $\pi^{*(j)}$ for $j = 1, \ldots, \mathfrak{C}$ is defined as a stationary state, thus satisfying:

$$\frac{dH^{(j)}\pi_i^{*(j)}}{dt} = 0, \qquad \frac{dH^{(j)}s^{*(j)}}{dt} = 0.$$

The Storage Function. A storage function $\mathfrak{B}$ is defined as

$$\mathfrak{B}^{(j)} = H^{(j)}\left[-s^{(j)} + s^{*(j)} + \sum_{i=1}^{\mathcal{K}+1} A_i(\pi^{*(j)})\left(\pi_i^{(j)} - \pi_i^{*(j)}\right)\right] \tag{46}$$

and

$$\mathfrak{B} = \sum_{j=1}^{\mathfrak{C}} \mathfrak{B}^{(j)}, \tag{47}$$

where s denotes entropy density, that is, volume-specific entropy. The properties of Eqs. 46 and 47 are summarized in the following Lemma:

Lemma 1. $\mathfrak{B}^{(j)}$, and therefore $\mathfrak{B}$, are convex functions of the elements of the vector $\pi^{(j)}$. Moreover, $\mathfrak{B}^{(j)} \geq 0$ with equality at $(\pi^{*(j)}, s^{*(j)})$.

Proof. Convexity follows from the construction of $\mathfrak{B}$ and from the concavity property of the entropy density $s^{(j)}$. To show that $\mathfrak{B}$ is nonnegative, we note that from the concavity of $s^{(j)}$:

$$s^{(j)} \leq s^{*(j)} + \sum_{i=1}^{\mathfrak{K}+1} \left(\frac{\partial s^{(j)}}{\partial \pi_i^{(j)}} \right)^{*} \left(\pi_i^{(j)} - \pi_i^{*(j)} \right) \tag{48}$$

and

$$A_i^{*(j)} = \left(\frac{\partial s^{(j)}}{\partial \pi_i^{(j)}} \right)^{*}.$$

Comparing Eqs. 46 and 48, the result follows.

A balance equation can be derived for $\mathfrak{B}$ in the same way as we did with Eq. 19:

$$\frac{d\,\mathfrak{B}^{(j)}}{dt} = - \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \frac{dH^{(j)} \overline{\pi}_i^{(j)}}{dt},$$

where $\overline{A}_i^{(j)} = A_i^{(j)} - A_i^{*(j)}$ and $\overline{\pi}_i^{(j)} = \pi_i^{(j)} - \pi_i^{*(j)}$. Using Eq. 10, we get

$$\begin{aligned} \frac{d\,\mathfrak{B}^{(j)}}{dt} = & - \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \overline{F}_{\pi\,\mathrm{in}}^{(j)} + \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \upsilon^{(j)} \overline{\pi}_i^{(j)} \\ & - \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \overline{\psi}_{\pi_i t}^{(jk)} - \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \overline{\psi}_{\pi_i s}^{(j)}. \end{aligned} \tag{49}$$

Summation over all regions leads to

$$\begin{aligned} \frac{d\,\mathfrak{B}}{dt} = & - \sum_{j=1}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \overline{F}_{\pi\,\mathrm{in}}^{(j)} + \sum_{j=1}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \upsilon^{(j)} \overline{\pi}_i^{(j)} \\ & - \sum_{j=1, j \neq k}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \left(\overline{A}_i^{(j)} - \overline{A}_i^{(k)} \right) \overline{\psi}_{\pi_i t}^{(jk)} - \sum_{j=1}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \overline{\psi}_{\pi_i s}^{(j)}. \end{aligned} \tag{50}$$

It is noted that the first and last terms on the righthand side generally have an indefinite sign. The third term on the righthand side is associated to the *transfer rates* and has a *negative sign* as stated by the following lemma.

Lemma 2. The righthand term

$$\sum_{j=1, j \neq k}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \left(\overline{A}_i^{(j)} - \overline{A}_i^{(k)} \right) \overline{\psi}_{\pi_i t}^{(jk)}$$

in Eq. 50 is nonnegative definite.

Proof. This can be shown by noting that from the Onsager relations:

$$\overline{\psi}_{\pi_i \mathrm{transfer}}^{(jk)} = \sum_{m=1}^{\mathfrak{K}+1} \ell_{im}^{jk} \left(\overline{A}_m^{(j)} - \overline{A}_m^{(k)} \right)$$

with $L > 0$, then

$$\sum_{j=1, j \neq k}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \left(\overline{A}_i^{(j)} - \overline{A}_i^{(k)} \right) \overline{\psi}_{\pi_i t}^{(jk)} \geq 0. \tag{51}$$

From Corollary 1, $\sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \upsilon^{(j)} \overline{\pi}_i^{(j)} = \upsilon^{(j)} \overline{A}^{T} \overline{\pi} \leq 0$, thus ensuring negative definiteness of the third term on the righthand side of Eq. 50.

Next, the structural stability of an exchange plant with the convective matrix given in Eq. 45 is established.

Proposition 1. Assume that an exchange plant with the convective matrix in Eq. 45, $\overline{F}_{\pi\,\mathrm{in}}^{(j)} = 0$, and that no sources are present, that is, $\psi_{\pi_i \mathrm{source}}^{(j)} = 0$. Then $\pi^{(j)} \rightarrow \pi^{*(j)}$ everywhere in $j = 1, \ldots, \mathfrak{C}$. Moreover, locally the convergence is of exponential type.

Proof. First, let us write Eq. 49 as

$$\mathfrak{B}(t + \tau) - \mathfrak{B}(t) = - \int_{t}^{t+\tau} \left(g_1(s) + g_2(s) \right) ds$$

with

$$g_1(t) = - \sum_{j=1}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \overline{A}_i^{(j)} \upsilon^{(j)} \overline{\pi}_i^{(j)} \geq 0 \tag{52}$$

$$g_2(t) = \sum_{j \neq k}^{\mathfrak{C}} \sum_{i=1}^{\mathfrak{K}+1} \left(\overline{A}_i^{(j)} - \overline{A}_i^{(k)} \right) \overline{\psi}_{\pi_i t}^{(jk)} \geq 0. \tag{53}$$

Since $\mathfrak{B}(t) \geq 0 \; \forall t > 0$ and $g_1(t)$ and $g_2(t)$ are positive definite:

$$\infty > \int_{t}^{t+\tau} g_1(s) + g_2(s)\, ds \geq 0,$$

where $\mathfrak{B}(t)$ is uniformly continuous; Barbalat's lemma applies (Slotine and Li, 1991), and therefore

$$g_1(t) \rightarrow 0$$

$$g_2(t) \rightarrow 0,$$

which implies that $\pi^{(j)} \rightarrow \pi^{*(j)}$.

Lyapunov arguments can be employed in the vicinity of the stationary reference to show asymptotic convergence to the stationary state. We therefore note that close to equilibrium $\overline{A}^{(j)}$ can be approximated by a first-order series expansion (Eq. 41):

$$\overline{A}^{T(j)} = \overline{\pi}^{T(j)} M, \tag{54}$$

with M defined in Eq. 42, and therefore

$$\frac{d\,\mathcal{B}^{(j)}}{dt} = -\,\bar{\pi}^{T(j)} M \frac{d\bar{\pi}^{(j)}}{dt}$$

$$\bar{A}^{T(j)} \bar{\pi}^{(j)} = \bar{\pi}^{T(j)} M \bar{\pi}^{(j)}. \tag{55}$$

Defining a function

$$\mathcal{V} = -\,\bar{\pi}^{T(j)} M \bar{\pi}^{(j)} \geq 0,$$

we can write Eq. 49 as

$$\frac{d\mathcal{V}^{(j)}}{dt} + \upsilon^{(j)} \mathcal{V}^{(j)} \leq -\sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \bar{F}_{\pi\,\mathrm{in}}^{(j)}, \tag{56}$$

where the sources are assumed to be zero. The inequality comes from the positive definite sign for $g_2(t)$ (term produced by property transfer). Fixing the input convective flows in Eq. 56 to be equal to zero, it is easy to show that

$$\mathcal{V}^{(j)}(t) \leq \mathcal{V}^{(j)}(0) \exp(-\lambda t),$$

where λ is some positive constant. Therefore, $\mathcal{V}^{(j)} \to 0$ and $\bar{\pi}^{(j)} \to 0$ exponentially.

The same argument can be employed for a system consisting of $\mathcal{C}$ regions, since

$$\mathcal{V}(t) = \sum_{j=1}^{\mathcal{C}} \mathcal{V}^{(j)}(t).$$

Exchange-Equilibrium Plants with Kirchhoff Convection

The concept of binary exchange-equilibrium plants (Hangos and Perkins, 1997) is extended in this section to construct a more general class of process plants: the (multicomponent) exchange-equilibrium plants with Kirchhoff convection. The structural stability of such plants is then analyzed.

Definition 1. A process plant satisfying basic assumptions is called an exchange-equilibrium plant with Kirchhoff convection if

- There is no source term ($\psi_{\pi_i s}^{(j)}$) in any of Eqs. 10,
- There are only Kirchhoff convective transport, exchange, and equilibrium relations taking place in the system

for every $\varphi^{(j)} \in \mathfrak{X}^{(j)}$, $j = 1, \ldots, \mathcal{C}$.

In other words, only Kirchhoff convective transport and transfer processes with equilibrium take place in an exchange-equilibrium plant with Kirchhoff convection.

Storage function of exchange-equilibrium plants with Kirchhoff convection

In order to investigate the stability of exchange-equilibrium plants with Kirchhoff convection, the properties of their storage function should be determined.

The storage function $\mathcal{B}^{(j)}$ of region j is a special case of Eq. 49:

$$\frac{d\,\mathcal{B}^{(j)}}{dt} = -\sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \bar{F}_{\pi_i \mathrm{in}}^{(j)} + \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \upsilon^{(j)} \bar{\pi}_i^{(j)} - \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \bar{\psi}_{\pi_i t}^{(jk)}. \tag{57}$$

Summation over all regions leads to the overall storage function $\mathcal{B}$ in a form analogous to Eq. 50:

$$\frac{d\,\mathcal{B}}{dt} = -\sum_{j=1}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \bar{F}_{\pi_i \mathrm{in}}^{(j)} + \sum_{j=1}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \upsilon^{(j)} \bar{\pi}_i^{(j)} - \sum_{j \neq k}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \left(\bar{A}_i^{(j)} - \bar{A}_i^{(k)} \right) \bar{\psi}_{\pi_i t}^{(jk)}. \tag{58}$$

The preceding form of the overall storage function is simplified using Eqs. 21–25 to express Kirchhoff convection conditions. These equations enable us to combine the first two convective terms in Eq. 58 to obtain:

$$\frac{d\,\mathcal{B}}{dt} = -\sum_{j=1}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \upsilon^{(j)} \left(\sum_{\ell=1}^{\mathcal{C}} \alpha_\ell^{(j)} \bar{\pi}_i^{(\ell)} + \alpha_0^{(j)} \bar{\pi}_{iB}^{(j)} - \bar{\pi}_i^{(j)} \right) - \sum_{j \neq k}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \left(\bar{A}_i^{(j)} - \bar{A}_i^{(k)} \right) - \bar{\psi}_{\pi_i t}^{(jk)}. \tag{59}$$

Structural stability of exchange-equilibrium plants with Kirchhoff convection

Before analyzing the structural stability, it is important to recall the notion of structural stability. A system is called *structurally stable* if it is stable for all possible values of its parameters that leave the system structure, (i.e., the functional form of the dynamic model equations and its dynamic variables) unchanged. Stability is understood here to denote asymptotic stability as defined in systems and control theory (Kailath, 1980).

In analyzing the structural stability of exchange-equilibrium process plants with Kirchhoff convection, it is important that the time derivative of their storage function, in the form of Eq. 59, can be decomposed into three additive parts:

$$\frac{d\,\mathcal{B}}{dt} = \mathcal{B}_t^{\mathrm{conv}} + \mathcal{B}_t^{\mathrm{transfer}} + \mathcal{B}_t^{\mathrm{in}}$$

with

$$\mathcal{B}_t^{\mathrm{conv}} = -\sum_{j=1}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \tilde{C}_{\mathcal{C}} \bar{\pi}_i^{(j)} \tag{60}$$

$$\mathcal{B}_t^{\mathrm{in}} = -\sum_{j=1}^{\mathcal{C}} \sum_{i=1}^{\mathcal{K}+1} \bar{A}_i^{(j)} \upsilon^{(j)} \alpha_0^{(j)} \bar{\pi}_{iB}^{(j)} \tag{61}$$

and

$$\mathcal{B}_t^{\text{transfer}} = - \sum_{j \neq k}^{\mathfrak{C}} \sum_{i=1}^{\mathcal{K}+1} \left(\bar{A}_i^{(j)} - \bar{A}_i^{(k)} \right) \bar{\psi}_{\pi_i t}^{(jk)} \tag{62}$$

with the following convective coefficient matrix

$$\tilde{C}_{\mathfrak{C}} = \begin{bmatrix} -\left(1 - \alpha_1^{(1)}\right) v^{(1)} & \alpha_1^{(2)} v^{(2)} & \cdots & \alpha_1^{(\mathfrak{C})} v^{(\mathfrak{C})} \\ \cdots & \cdots & \cdots & \cdots \\ \alpha_{\mathfrak{C}}^{(1)} v^{(1)} & \alpha_{\mathfrak{C}}^{(2)} v^{(2)} & \cdots & -\left(1 - \alpha_{\mathfrak{C}}^{(\mathfrak{C})}\right) v^{(\mathfrak{C})} \end{bmatrix}. \tag{63}$$

Note: $\tilde{C}_{\mathfrak{C}}$ is a Kirchhoff convection submatrix and therefore negative semidefinite.

The term B_t^{in} describes the effect of the inlet to the whole process system, which is an *input* in the system theoretical sense; therefore, it does *not* affect its structural stability. Thus $\bar{\pi}_{iB}^{(j)} = 0$ can be assumed for the stability analysis.

It already has been shown that the transfer term is negative definite, that is, $\mathcal{B}_t^{\text{transfer}} \leq 0$ (see Eq. 51). Therefore structural stability of exchange-equilibrium plants depends on the sign of the convective term $\mathcal{B}_t^{\text{conv}}$ that contains *both* the input and output convective terms internal to the process system.

We use Corollary 1 to express the convective term in a compact form for later use (see the Appendix), and write $\bar{A}^{(j)}$ as

$$\bar{A}^{(j)} = Q^{(j)} \bar{\pi}^{(j)}, \tag{64}$$

where, as demonstrated, $Q^{(j)}$ is negative definite for each region j. Let us first define the following vectors, which will be used next:

$$\bar{\mathfrak{A}} = \left[\bar{A}^{T(1)}, \ldots, \bar{A}^{T(j)}, \ldots, \bar{A}^{T(\mathfrak{C})} \right]^T$$

$$\bar{\Pi} = \left[\bar{\pi}^{T(1)}, \ldots, \bar{\pi}^{T(j)}, \ldots, \bar{\pi}^{T(\mathfrak{C})} \right]^T.$$

Equation 60 can be written in compact form as

$$\mathcal{B}_t^{\text{conv}} = - \bar{\mathfrak{A}}^T \left(\tilde{C}_{\mathfrak{C}} \otimes I_{(\mathcal{K}+1 \times \mathcal{K}+1)} \right) \bar{\Pi}, \tag{65}$$

where $\otimes$ represents the Kronecker product and $I_{(\mathcal{K}+1 \times \mathcal{K}+1)}$ is a $\mathcal{K}+1 \times \mathcal{K}+1$-dimension unit matrix. We recall that the Kronecker product of two matrices A and B is of the form:

$$A \otimes B = \begin{bmatrix} a_{11} B & a_{12} B & \cdots & a_{1n} B \\ \cdots & a_{22} B & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ a_{m1} B & a_{m2} B & \cdots & a_{mn} B \end{bmatrix}$$

and that if A and B are n-dimensional square matrices with eigenvalues $\{\lambda_1, \ldots, \lambda_n\}$ and $\{\mu_1, \ldots, \mu_n\}$, respectively, the eigenvalues of $A \otimes B$ are $\{\lambda_i \mu_j\}$ for $i, j = 1, \ldots, n$ (Korn and Korn, 1968).

Using Eq. 64, vector $\bar{\mathfrak{A}}$ can be written as

$$\bar{\mathfrak{A}} = \begin{bmatrix} Q^{(1)} & 0 & \cdots & 0 & 0 \\ 0 & \cdots & Q^{(j)} & \cdots & 0 \\ 0 & \cdots & \cdots & 0 & Q^{(\mathfrak{C})} \end{bmatrix} \bar{\Pi}.$$

Substituting this equation into Eq. 65, the following important Lemma is obtained.

Lemma 3. The convective term in the overall storage function (Eq. 59) of exchange-equilibrium plants with Kirchhoff convection can be expressed as

$$\mathcal{B}_t^{\text{conv}} = - \bar{\Pi}^T \mathcal{P} \bar{\Pi} \tag{66}$$

with

$$\mathcal{P} = \begin{bmatrix} Q^{T(1)} & \cdots & 0 \\ \cdots & Q^{T(j)} & \\ \cdots & \cdots & Q^{T(\mathfrak{C})} \end{bmatrix} \left(\tilde{C}_{\mathfrak{C}} \otimes I_{(\mathcal{K}-1 \times \mathcal{K}+1)} \right),$$

and is negative semidefinite.

Proof. Matrix $\mathcal{P}$ can be expressed as

$$\mathcal{P} = \sum_{j=1}^{\mathfrak{C}} \tilde{C}_{\mathfrak{C}} \otimes Q^{T(j)}.$$

Since matrix $\tilde{C}_{\mathfrak{C}}$ is negative semidefinite (see Lemma 7 in the Appendix) and $Q^{T(j)}$ are negative definite (Corollary 1 in the Appendix), their eigenvalues are nonpositive. Using the eigenvalue property of Kronecker product, reported previously, it follows that $\mathcal{P}$ is positive semidefinite and $\mathcal{B}_t^{\text{conv}} \leq 0$.

Proposition 2. Assume with an exchange-equilibrium plant with Kirchhoff convection, that is a convective matrix Eq. 63, $\bar{F}_{\pi\text{in}}^{(j)} = 0$ and no sources are present, that is, $\psi_{\pi_i s}^{(j)} = 0$. Then $\pi^{(j)} \rightarrow \pi^{*(j)}$ everywhere in $j = 1, \ldots, \mathfrak{C}$. Moreover, locally the convergence is exponential.

Proof. Using $g_1(t) = \bar{\Pi}^T \mathcal{P} \bar{\Pi}$, the result follows from the same line of arguments as in Proposition 1.

It is important to note that the convective part goes to zero but does not necessarily imply convergence to the reference state. It is the negative definiteness of the transfer part that ensures convergence.

Examples

The following cases are treated in the next subsection.

1. When only the energy balance needs to be considered, there is only one component present in each region. Heat-exchanger networks belong in this category.
2. There is only a single region present in the process system. A good example is a multicomponent flash.
3. The system contains only ideal mixtures and is isothermal, or it is assumed that only component mass balances are present. A distillation column with constant molar flows and ideal mixtures represents this case.

Heat-exchanger networks

Heat-exchanger networks can be regarded as the simplest process systems satisfying our basic assumptions, where only the energy transport equations form the engineering model. In other words, $\mathfrak{K} = 0$, that is, only one extensive conserved quantity, the internal energy $E^{(j)}$, is considered in each region.

Heat-exchanger networks are known to be structurally asymptotically stable (Hangos and Perkins, 1997).

Conservation Balances. A heat-exchanger cell is a pair of regions connected by a heat-conducting wall. With our basic assumptions the engineering model of the jth region connected to the ℓth one and together form a heat exchanger cell that can be written in the same form as the energy transport equation for the volume-specific energies $(\bar{e}^{(j)}, \bar{e}^{(\ell)})$ of the region around the operation point $(e^{(j)*}, e^{(\ell)*})$ as follows:

$$\frac{d\bar{e}^{(j)}}{dt} = \left(\sum_{k=1}^{\mathfrak{C}} \left[\alpha_k^{(j)} \bar{e}^{(k)} \right] + \alpha_0^{(j)} \bar{e}_B^{(j)} \right) - \upsilon^{(j)} \bar{e}^{(j)} + \bar{\psi}_t^{(j\ell)} \tag{67}$$

$$\frac{d\bar{e}^{(\ell)}}{dt} = \left(\sum_{k=1}^{\mathfrak{C}} \left[\alpha_k^{(\ell)} \bar{e}^{(k)} \right] + \alpha_0^{(\ell)} \bar{e}_B^{(\ell)} \right) - \upsilon^{(\ell)} \bar{e}^{(\ell)} - \bar{\psi}_t^{(j\ell)}. \tag{68}$$

With our basic assumptions the following relation holds between the volume-specific energy and temperature of a region:

$$e^{(j)} = c_P \rho T^{(j)} + e_0 \tag{69}$$

where the specific heat c_P and the density ρ are constant for every region, and e_0 is an arbitrary reference. Note that only one component (actually, usually water) is present in each region, so there is no need for component balances.

Stability Analysis of Heat-Exchanger Networks. We use Eq. 46 for stability analysis, and note that it is additive over the total number of heat exchanger cells N. This implies

$$\mathfrak{B} = \sum_{j=\ell=1}^{N} \mathfrak{B}^{(j\ell)}.$$

We obtain each term $[d\,\mathfrak{B}^{(j\ell)}/dt]$ by multiplying Eqs. 67 and 68 by the corresponding intensive property $\bar{A}_1$ of internal energy in ℓ and j. For this case,

$$\bar{A}^{(k)} = \left(\frac{1}{T^{(k)}} - \frac{1}{T^{(k)*}} \right) \tag{70}$$

and

$$\frac{d\,\mathfrak{B}^{(j\ell)}}{dt} = \mathfrak{B}_t^{\text{conv}(j)} + \mathfrak{B}_t^{\text{transfer}(j\ell)}, \tag{71}$$

assuming there is no change in the internal energies of the inlet when compared to the reference value, that is, $\bar{e}_B^{(j)} = 0$, $j = 1, \ldots, \mathfrak{C}$.

From Onsager relations, the terms $\mathfrak{B}_t^{\text{transfer}(j\ell)} \leq 0$ (see the general equation, Eq. 51). Summation over the N heat-exchanger cells gives

$$\frac{d\,\mathfrak{B}}{dt} = \sum_{j=\ell=1}^{N} \frac{d\,\mathfrak{B}^{(j\ell)}}{dt} = \sum_{j=1}^{2N} \mathfrak{B}_t^{\text{conv}(j)} + \sum_{j=\ell=1}^{N} \mathfrak{B}_t^{\text{transfer}(j\ell)}. \tag{72}$$

The convective term $\sum_{j=1}^{2N} \mathfrak{B}_t^{\text{conv}(j)}$ can be written in matrix notation as

$$\mathfrak{B}_t^{\text{conv}(j)} = -\, \bar{\mathfrak{A}}^{T} \tilde{C}_{\mathfrak{C}}\, \bar{e}, \tag{73}$$

where

$$\bar{e}^T = \left[\bar{e}^{(1)}, \ldots, \bar{e}^{(\ell)}, \ldots, \bar{e}^{(2N)} \right]$$

and the corresponding intensive properties are:

$$\bar{\mathfrak{A}}^{T} = \left[\bar{A}^{(1)}, \ldots, \bar{A}^{(\ell)}, \ldots, \bar{A}^{(2N)} \right].$$

The matrix $\tilde{C}_{\mathfrak{C}}$ is the Kirchhoff convection submatrix describing the flow structure of the heat-exchanger network in the form of Eq. 63; it is negative semidefinite.

Next we develop the actual form of the matrix M for Eq. 54. For this, Eq. 70 can be used together with Eqs. 64 and 69. Expanding Eq. 70 into a Taylor series around the operation point $T^{*(k)}$ and using Eq. 69, we get for the diagonal elements:

$$[M^*]_{kk} = -\frac{C_P \rho}{\left(T^{*(k)}\right)^2} < 0, \tag{74}$$

and all the off-diagonal elements are equal to zero, that is, M *is diagonal and negative definite* in this case. Using the results of the section on stability analysis of process systems via passivity theory, the following Lemma results.

Lemma 4. Heat-exchanger networks with Kirchhoff convection are structurally asymptotically stable.

Note that M and $\tilde{C}_{\mathfrak{C}}$ can be commuted in this case; therefore, the result immediately follows from Eqs. 74 and 73.

Multicomponent flash with constant molar flows

It has been shown by Rouchon and Creff (1993) that a multicomponent flash with constant molar flows is structurally asymptotically stable.

Engineering Model of the Multicomponent Flash. First, consider a multicomponent flash with constant molar flows of liquid feed F_L and vapor feed F_V, and liquid and vapor outflow $\mathcal{L}$ and $\mathcal{V}$, respectively. The external heat supply is represented by the term Q. If we denote the mole fraction of component k in the liquid phase by ξ_k and that in the vapor phase by η_k with the constant molar holdups $H^{(L)}$ and $H^{(V)}$ in the liquid and vapor phases, respectively, the following dynamic balance equations result:

Component mass balances, $k = 1, \ldots, \mathcal{K}$

$$(L) \quad H^{(L)} \frac{d\xi_k}{dt} = F_L \xi_{Bk} - \mathfrak{L}\xi_k - \psi_{kt}$$

$$(V) \quad H^{(V)} \frac{d\eta_k}{dt} = F_V \eta_{Bk} - \mathfrak{V}\eta_k + \psi_{kt}. \tag{75}$$

Energy balances

$$(L) \quad H^{(L)} \frac{de^{(L)}}{dt} = F_L h_L(T_{FL}, \xi_{Fk};\ k = 1, \ldots, \mathcal{K}) - \mathfrak{L}\, h_L(T_L, \xi_k;\ k = 1, \ldots, \mathcal{K}) - Q_\psi + Q$$

$$(V) \quad H^{(V)} \frac{de^{(V)}}{dt} = F_V h_V(T_{FV}, \eta_{Fk};\ k = 1, \ldots, \mathcal{K}) - \mathfrak{V}\, h_V(T_V, \eta_k;\ k = 1, \ldots, \mathcal{K}) + Q_\psi. \tag{76}$$

Constitutive equations

$$\sum_{k=1}^{\mathcal{K}} \xi_k = 1, \qquad \sum_{k=1}^{\mathcal{K}} \eta_k = 1, \qquad \sum_{k=1}^{\mathcal{K}} \psi_k = \Psi \tag{77}$$

$$\psi_{kt} = L_{c_k c_k}\left(\frac{\mu_k^{(L)}}{T^{(L)}} - \frac{\mu_k^{(V)}}{T^{(V)}}\right) \tag{78}$$

$$Q_\psi = L_{TT}\left(\frac{1}{T^{(V)}} - \frac{1}{T^{(L)}}\right) \tag{79}$$

$$e^{(X)} = c_{PX} T^{(X)} + e_0^{(X)}, \qquad X = L, V \tag{80}$$

$$h_L(T, \xi_k;\ k = 1, \ldots, \mathcal{K}) = h_L T + h_0^L,$$
$$h_V(T, \eta_k;\ k = 1, \ldots, \mathcal{K}) = h_V T + h_0^V, \tag{81}$$

where h_V and h_L are specific energy; T_{FV} and T_{FL} are the feed temperature; $\mu_k^{(V)}$ and $\mu_k^{(L)}$ are the chemical potential of the kth component of the vapor and liquid phases, respectively; $e_0^{(X)}$, h_0^L, and h_0^V represent arbitrary references; and Q and Q_ψ are the external energy source and the evaporation energy, respectively.

Stability Analysis of the Multicomponent Flash. In the passivity analysis, we use the Onsager relationships for energy and component transfer, which take the form:

$$\Psi_{tr} = L\tilde{A},$$

with L a positive definite and symmetric matrix of constant coefficients, and $\tilde{A}$, Ψ_{tr} vectors of intensive variables and transfer rates, respectively, of the form:

$$\tilde{A} = \left[\left(\frac{1}{T^{(V)}} - \frac{1}{T^{(L)}}\right), \left(\left(\frac{\mu_k}{T}\right)^{(L)} - \left(\frac{\mu_k}{T}\right)^{(V)}\right);\ k = 1, \ldots, \mathcal{K}\right]^T$$

$$\Psi_{tr} = \left[Q_\psi, \psi_{kt};\ k = 1, \ldots, \mathcal{K}\right]^T.$$

The analysis is concerned with the structural stability of a certain stationary operation point, defined by the following set of steady-state mole and energy balances:

$$(L) \quad (F_L \xi_{Bk})^* - (\mathfrak{L}\xi_k)^* - \psi_{kt}^* = 0$$

$$(V) \quad (F_V \eta_{Bk})^* - (\mathfrak{V}\eta_k)^* + \psi_{kt}^* = 0.$$

$$(L) \quad F_L^* h_L(T_{FL}^*, \xi_{Fk}^*;\ k = 1, \ldots, \mathcal{K}) - \mathfrak{L}^* h_L\left(T^{*(L)}, \xi_k^*;\ k = 1, \ldots, \mathcal{K}\right) - Q_\psi^* = 0$$

$$(V) \quad F_V^* h_V(T_{FV}^*, \eta_{Fk}^*;\ k = 1, \ldots, \mathcal{K}) - \mathfrak{V}^* h_V\left(T^{*(V)}, \eta_k^*;\ k = 1, \ldots, \mathcal{K}\right) + Q_\psi^* = 0.$$

We note that for $(\xi_k^*, \eta_k^*, T^{*(V)}, T^{*(V)})$ to be an equilibrium point, the system must consist of constant molar flows that have no source, that is, the quantities $\overline{\mathfrak{L}}$, $\overline{\mathfrak{V}}$, $\overline{F}$, and Q all must be zero. In that case, the transfer-rate vector $\Psi_{tr}^* = 0$, and therefore:

$$\overline{\Psi}_{tr} = L\left[\left(A^{(V)} - A^{*(V)}\right) - \left(A^{(L)} - A^{*(L)}\right)\right],$$

with $A^{*(L)} = A^{*(V)} = A^{eq}$, where

$$A^{(X)} = \left[\left(\frac{1}{T^{(X)}}\right), -\left(\frac{\mu_k}{T}\right)^{(X)};\ k = 1, \ldots, \mathcal{K}\right]^T, \quad X = L, V.$$

For convenience, let ust denote the elements of $A^{(X)}$ as

$$A^{(X)} = \left[A_{1X}, A_{kX};\ k = 1, \ldots, \mathcal{K}\right]^T, \qquad X = L, V.$$

In the analysis, we use the results of the section on stability analysis of process systems via passivity theory and write a balance for $\mathcal{B}$ (Eqs. 46, 47, and 50), as

$$\frac{d\mathcal{B}}{dt} = \left(\overline{A}_1^{(L)} - \overline{A}_1^{(V)}\right)\overline{Q}_\psi + \sum_{k=1}^{\mathcal{K}} \left(\overline{A}_k^{(L)} - \overline{A}_k^{(V)}\right)\overline{\psi}_{kt} + \mathfrak{L}^*\left(\overline{A}_1^{(L)}\overline{h}_L + \sum_{k=1}^{\mathcal{K}} \overline{A}_k^{(L)}\overline{\xi}_k\right) + \mathfrak{V}^*\left(\overline{A}_1^{(V)}\overline{h}_V + \sum_{k=1}^{\mathcal{K}} \overline{A}_k^{(V)}\overline{\eta}_k\right),$$

where $\mathfrak{L}^*$ and $\mathfrak{V}^*$ are assumed to be constant. The right-hand side can be decomposed into a transfer part $\mathcal{B}_t^{\text{transfer}}$ (Eq. 62) and a convective part $\mathcal{B}_t^{\text{conv}}$ (Eq. 60). Comparing this equation with Eq. 50 and using Lemma 2, it follows that $\mathcal{B}_t^{\text{transfer}}$ is of the form:

$$\left(\overline{A}_{1L} - \overline{A}_{1V}\right)\overline{Q}_\psi - \sum_{k=1}^{\mathcal{K}} \left(\overline{A}_{kL} - \overline{A}_{kV}\right)\overline{\psi}_k = -\left(\overline{A}_V - \overline{A}_L\right)^T L\left(\overline{A}_V - \overline{A}_L\right) \le 0.$$

Using Eq. 55, it is shown that

$$\overline{A}_{1L}\overline{h}_L - \sum_{k=1}^{\mathcal{K}} \overline{A}_{kL}\overline{\xi}_k = \overline{A}_L^T \overline{\pi}_L \le 0$$

$$\overline{A}_{1V}\overline{h}_V - \sum_{k=1}^{\mathcal{K}} \overline{A}_{kV}\overline{\eta}_k = \overline{A}_V^T \overline{\pi}_V \le 0.$$

The following lemma results from this.

Lemma 5. The multicomponent flash with constant molar flows is structurally asymptotically stable.

Distillation column with constant molar flows and ideal mixtures in the nonequilibrium case

The stability of multicomponent distillation has been investigated by many authors over the years. A comprehensive article that covers most of the results for various operating condition is by Doherty and Perkins (1982).

If the equilibrium at the trays cannot be assumed, then dynamic balance equations describing the component transport both in the vapor phase and the liquid phase should be considered. Therefore two regions are needed for describing the behavior of a tray, one for the liquid and one for the vapor phase. The transfer between the phases is described by transfer-rate expressions.

Conservation Balances of the Distillation Tray. Because of the molar flow conditions, only the component transport equations for the volume-specific component mass of the components (that is, concentrations $c_k^{(jV)}$ and $c_k^{(jL)}$ on the jth tray in both phases have to be written in deviation form near an operating point:

$$H^{(jL)}\frac{d\bar{c}_k^{(jL)}}{dt} = \mathfrak{L}\left(\bar{c}_k^{[(j+1)L]} - \bar{c}_k^{(jL)}\right) + \bar{\psi}_t^{(j)},\qquad k = 1,\ \dots,\ \mathfrak{K} \tag{82}$$

$$H^{(jV)}\frac{d\bar{c}_k^{(jV)}}{dt} = \mathfrak{V}\left(\bar{c}_k^{[(j-1)V]} - \bar{c}_k^{(j)V}\right) - \bar{\psi}_t^{(j)},\qquad k = 1,\ \dots,\ \mathfrak{K}, \tag{83}$$

where $\mathfrak{L}$ and $\mathfrak{V}$ are the constant molar liquid and vapor flow rate, respectively.

Because of the isothermic conditions and ideality of the mixtures present, the following relation holds between the chemical potentials and the concentrations in each phase:

$$\mu_k^{(\ell)} = \mu_{k\,\ell}^0 + K^{(\ell)}\ln\left(c_k^{(\ell)}\right),\qquad \mu^{(\ell)} = \sum_{k=1}^{\mathfrak{K}}\mu_k^{(\ell)}, \tag{84}$$

where $K^{(\ell)}$ is a positive constant for each region.

Stability Analysis of the Distillation Column. Again we use Eq. 46, which is additive over the total number of distillation trays N:

$$\mathfrak{B} = \sum_{j=1}^{N}\mathfrak{B}^{(jL)} + \mathfrak{B}^{(jV)}.$$

Each term $(d\,\mathfrak{B}^{(jX)}/dt)$, $X = L, V$ is obtained by multiplying Eqs. 82 and 83 by their corresponding intensive properties $\bar{A}_k$ in regions jL and jV, which is in the form

$$\bar{A}_k^{(jX)} = \left[\ln\left(c_k^{(jX)}\right) - \ln\left(c_k^{(jX)*}\right)\right],\qquad k = 1,\ \dots,\ \mathfrak{K},\qquad X = L, V. \tag{85}$$

From Onsager relations, the term $\mathfrak{B}_t^{\text{transfer}(jX)} \le 0$ (see Eq. 51). Summation over the N trays (i.e., $2N$ regions) gives

$$\frac{d\,\mathfrak{B}}{dt} = \sum_{j=1}^{N}\mathfrak{B}^{(jL)} + \mathfrak{B}^{(jV)}$$

$$= \sum_{j=1}^{2N}\mathfrak{B}_t^{\text{conv}(j)} + \sum_{j=1}^{N}\mathfrak{B}_t^{\text{transfer}(jL)} + \mathfrak{B}_t^{\text{transfer}(jV)}. \tag{86}$$

The convective term $\sum_{j=1}^{2N}\mathfrak{B}_t^{\text{conv}(j)}$ can be written in matrix notation as:

$$\mathfrak{B}_t^{\text{conv}} = -\sum_{k=1}^{\mathfrak{K}}\bar{\mathfrak{A}}_k{}^T\tilde{C}_{D\mathfrak{C}}\,\bar{c}_k, \tag{87}$$

where

$$\bar{c}_k^T = \left[\bar{c}_k^{(1L)},\ \bar{c}_k^{(1V)},\ \dots,\ \bar{c}_k^{(NL)},\ \bar{c}_k^{(NV)}\right],\qquad k = 1,\ \dots,\ \mathfrak{K}$$

and the corresponding comprehensive properties are

$$\bar{\mathfrak{A}}_k^T = \left[\ \bar{A}_k^{(1L)},\ \bar{A}_k^{(1V)},\ \dots,\ \bar{A}_k^{(NL)}, \bar{A}_k^{(NV)}\right],\qquad k = 1,\ \dots,\ \mathfrak{K}.$$

The matrix $\tilde{C}_{D\mathfrak{C}}$ is a Kirchhoff convection submatrix describing the flow structure of the distillation column in the following form and is negative semidefinite:

$$\tilde{C}_{D\mathfrak{C}} = \begin{bmatrix} -\dfrac{L}{H_L} & 0 & \dfrac{L}{H_L} & 0 & \dots & 0 & 0 \\ 0 & -\dfrac{V}{H_V} & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & \dots & \dots & \dots & 0 & 0 \\ 0 & \dots & \dots & 0 & 0 & -\dfrac{L}{H_L} & 0 \\ 0 & \dots & \dots & 0 & -\dfrac{V}{H_V} & 0 & -\dfrac{V}{H_V} \end{bmatrix}. \tag{88}$$

Equation 85 can be used together with Eqs. 64 and 84 to show the actual form of matrix M_k. Expanding Eq. 85 into a Taylor series around the operation point $c_k^{*(j)}$ and using Eq. 84, for the diagonal elements we get

$$[M_k]_{jj} = -\frac{1}{c_k^{*(j)}} < 0,$$

and all the off-diagonal elements are equal to zero, that is, M_k is *diagonal and negative definite* in this case. Moreover, the terms in the sum (Eq. 87) do not interact with each other because the mixture is ideal.

From this, and using either the results of Lemma 3 or the fact that M is again commutative with $C_{D\mathfrak{C}}$, we obtain the following lemma.

Lemma 6. Distillation columns with constant molar flows, Kirchhoff convection, and ideal mixtures are structurally aymptotically stable.

Conclusions

In this article we investigated structural asymptotic stability of process plants without source terms. General results have been obtained by using novel analysis tools that take advantage of the underlying physical structure of the process systems. This refers to the properties of Kirchhoff convective matrices, together with the first and the second law of thermodynamics formalized on a passivity framework. It is our belief that the results presented will help in the development of systematic approaches to address design/control integration of large-scale plants.

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Appendix

Conservation matrices

Definition 2. A real square matrix $F = \{f_{ij}\}_{i,j=1}^{n}$ of order n is said to be a *column conservation matrix* (or *a row conservation matrix*) if it is a matrix with dominant main diagonal with respect columns (or rows), that is,

$$|f_{ii}| \geq \sum_{j \neq i} |f_{ij}| = R_i, \qquad i = 1, 2, \ldots, n \tag{A1}$$

or

$$|f_{ii}| \geq \sum_{j \neq i} |f_{ji}| = C_i, \qquad i = 1, 2, \ldots, n, \tag{A2}$$

and its elements have the following sign pattern

$$f_{ii} \leq 0, \qquad f_{ij} \geq 0, \qquad i \neq j \tag{A3}$$

In the case of a proper inequality for every inequality in either Eq. A1 or A2 F is said to be a strict column conservation matrix or a strict row conservation matrix.

Properties of Kirchhoff convection matrices

Kirchhoff convection matrices are special conservation matrices: they are *both* row and column conservation matrices. The following lemma states that Kirchhoff conservation matrices are negative semidefinite matrices.

Lemma 7. If a real square matrix $A = \{a_{ij}\}_{i,j=1}^{n}$ of order n is both a row and column conservation matrix, that is,

$$\sum_{j=1}^{n} a_{ij} = 0, \qquad \forall 1 \leq i \leq n, \tag{A4}$$

$$\sum_{i=1}^{n} a_{ij} = 0, \qquad \forall 1 \leq j \leq n, \tag{A5}$$

$$a_{ii} < 0, \qquad a_{ij} \geq 0, \qquad \forall i \neq j, \qquad 1 \leq i \leq n, \tag{A6}$$

then it is negative semidefinite, that is,

$$x^T A x \leq 0 \tag{A7}$$

for all real vector $x = [x_1, \ldots, x_n]^{\mathrm{T}}$.

Proof. In the case of $n = 2$, the matrix A is in the form of

$$A = \begin{bmatrix} -a & a \\ a & -a \end{bmatrix},$$

where $a > 0$ and the statement is equivalent to the well-known inequality between the arithmetic and geometric means:

$$x_1 x_2 \leq \frac{x_1^2 + x_2^2}{2}.$$

The preceding inequality is used to prove the statement in the general $n \geq 3$ case for the pairs (x_i, x_j) as follows. The elements in the main diagonal can be written in the form of

$$a_{ii} = -\frac{1}{2}\left(\sum_{j\neq i} a_{ji} + \sum_{j\neq i} a_{ij}\right).$$

With the preceding equation,

$$\begin{aligned} x^TAx &= \sum_{1\le i,j\le n} a_{ij}x_ix_j \\ &= \sum_{i\neq j} a_{ij}x_ix_j + \sum_i a_{ii}x_i^2 \\ &\le \sum_{i\neq j} a_{ij}\frac{x_i^2+x_j^2}{2} - \frac{1}{2}\Sigma_i\left(\sum_{j\neq i} a_{ji} + \sum_{j\neq i} a_{ij}\right)x_i^2 \\ &= \sum_i\sum_{j\neq i}\left(\frac{a_{ij}}{2}+\frac{a_{ij}}{2}\right)x_i^2 - \frac{1}{2}\sum_i\sum_{j\neq i}(a_{ji}+a_{ij})x_i^2 \\ &= 0. \end{aligned}$$

This means that the inequality $x^TAx \le 0$ holds for every real vector x.

Note that the analog statements do not hold for complex vectors x, even in the case of $n = 2$. For example, if $x_1 = 1 + i$ and $x_2 = 1 - i$, then $x_1x_2 = 2$ and $x_1^2 + x_2^2 = 0$.

Kirchhoff convection submatrices

If both the jth column and row are deleted from a Kirchhoff convection matrix, then a Kirchoff convection submatrix results. More precisely, any submatrix of a Kirchhoff convection matrix specified by a joint set of row and column indices forms a Kirchhoff submatrix.

Because of the construction, Kirchhoff convection submatrices are also both row and column conservation matrices. Therefore the following simple corollary of Lemma 7 holds.

Lemma 8. Kirchhoff convection submatrices are negative semidefinite.

The proof follows the same reasoning as that for Lemma 7.

Basic lemma for the structural stability result

Lemma 9. Let π^* be an arbitrary and possibly time-dependent reference vector value for intensive variables π with A being its corresponding potential. Then

$$g(\pi) = (A^T - A^{*T})(\pi - \pi^*) \le 0,$$

with equality at $\pi = \pi^*$ and $g(\pi) \le 0$.

Proof. We note that $g(\pi)$ can be written as

$$g(\pi) \le -\mathcal{B} - (A^T - A^{*T})\pi^*. \tag{A8}$$

Now, choose an arbitrary value π'. From the convexity of the storage function $\mathcal{B}$, it follows that:

$$\mathcal{B}(\pi') - \left[A^T(\pi') - A^T(\pi^*)\right](\pi - \pi') \le \mathcal{B}(\pi), \tag{A9}$$

where the preceding inequality (Eq. A9) is valid for all π' and π. Substituting

$$\mathcal{B}(\pi') = -\left[A^T(\pi') - A^T(\pi^*)\right]\pi'$$

into the same inequality, it becomes

$$\left[A^T(\pi') - A^T(\pi^*)\right]\pi \ge -\mathcal{B}(\pi) \qquad \forall\pi' \text{ and } \pi.$$

In particular, this inequality is true for $\pi = \pi^*$, so

$$\left[A^T(\pi') - A^T(\pi^*)\right]\pi^* \ge -\mathcal{B}(\pi^*) = 0 \qquad \forall\pi', \tag{A10}$$

where Lemma 1 in the subsection titled "Stability analysis of process systems via passivity theory" is applied. Then

$$g(\pi) = -\mathcal{B} - (A^T - A^{*T})\pi^* \le 0,$$

with equality if and only if $\pi = \pi^*$.

Corollary 1. For the Hessian matrix M defined in Eq. 13 for the vector of intensive variables π, there exists a negative definite matrix Q of the form:

$$Q = \int_0^1 M(\pi + \epsilon p)\, d\epsilon,$$

where p is an arbitrary vector and $\epsilon \in [0, 1]$, such that

$$g(\pi) = (\pi^T - \pi^{*T})Q(\pi - \pi^*).$$

Proof. Applying Netown's theorem for vectorial fields (Dennis and Schnable, 1983) to $A(\pi)$, we obtain

$$A(\pi) - A(\pi^*) = \left[\int_0^1 M(\pi + \epsilon p)\, d\epsilon\right](\pi - \pi^*),$$

where M is defined as in Eq. 13 and p is an arbitrary vector. Integration is carried out elementwise, with ϵ a scalar parameter lying in the interval [0, 1]. Let us define a matrix Q as

$$Q = \int_0^1 M(\pi + \epsilon p)\, d\epsilon. \tag{A11}$$

From Lemma 9 we have

$$g(\pi) = (A^T - A^{*T})(\pi - \pi^*) = (\pi - \pi^*)^TQ(\pi - \pi^*) \le 0,$$

with equality if and only if $\pi = \pi^*$. Therefore, Q is negative definite and the result follows.

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