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Towards A General Stability Analysis of Process Network Systems *

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Abstract: This paper considers process systems whose dynamics are described by conservation laws for extensive variables and second law of thermodynamics and which can also been considered as interconnected (network) systems. In representing the dynamics and the analysis of network systems Tellegen's theorem and the passivity theory are used. Different from the usual application of these two methods on large scale systems, in this work, we only consider a single unit (node). For a single process unit, we apply the Tellegen's theorem and using a suitable storage function, derive the expression for the rate of change of the storage function. This expression is obtained for the cases of single phase and binary phases.

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Keywords: process networks, stability, dissipation, network theory, irreversible thermodynamics.

1. INTRODUCTION

Chemical process systems can be viewed as a network consisting of interconnected processes with mixing reaction and separation. Such subsystems interact with each other via exchange of energy, mass, momentum and information, operating at different timescales and governed by thermodynamic laws. Analysis of system theoretical properties, control and optimization of these systems have been the subject of research for quite some time (Gilles, 1998; Hangos et al., 1999; Kumar and Daoutidis, 2002; Liu et al., 2011).

Network theory was originally developed for the analysis of electric circuits. In network theory, Tellegen's theorem plays an important role since it forms the foundation of several theorems for the energy distribution in the circuit theory (Penfield et al., 1970). For an electric network with a given topology consisting of nodes and edges between nodes, Tellegen's theorem is derived from conservation of current (flow) and uniqueness of the potentials at the nodes. Potential difference provide driving force for flow. The strength of Tellegen's theorem is its generality. It can be applied to any network provided the topology is known. Due to this generality. it has been extended to general thermodynamic, reaction and process systems (Oster et al., 1973; Oster and Perelson, 1973, 1974; Peusner, 1981; Mikulecky, 2001; Jillson and Ydstie, 2005, 2007; Wartmann and Ydstie, 2009). In these applications the corresponding flows obey local conservations laws and uniquesness of potentials.

Stability and control of networks can be addressed using the passivity theory and the application of passivity can provide for design of decentralised controllers. This is motivated by the property that the interconnection of passive subsystems result in a passive system. Passivity theory requires a storage function which is an indication of the energy in the system and it is used to derive sufficient conditions for a stable network under decentralised feedback control. A storage function (availability function) suitable for chemical processes has been proposed in Alonso and Ydstie (1997, 2001) and the conditions for which the process systems are dissipative have been studied.

In this work, we take a bottom-up approach and apply the passivity theory together with the Tellegen's theorem to a process represented by a single node in the process network context. Our main goal is to derive the sufficient conditions for passivity of single and multiphase systems. Therefore, this paper focuses on deriving an expression for the rate of change of the storage (availability) function.

This paper is organized as follows. Section 2 presents the problem statement. In Section 3, we define systems that are considered and provide necessary definitions and theorems. Section 4 states the passivity theory and describes the availability function used as a storage function for thermodynamic systems. This section also presents the expression for the rate of change of availability function for the single unit (node) case. In Section 5, we state our conclusions and future work.

2. PROBLEM STATEMENT

In this paper, we address the question, "Does there exist a general stability analysis for process networks consisting of multicomponent, multiphase subunits with phase equilib-

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rium?". Here, the equilibrium means that net flow of mass and energy between the phases is equal to zero. A first step to answer this question is to come up with a suitable storage function (Lyapunov function) and derive the rate of change of this function. To this end, we are going to make use of the passivity, graph theory, Tellegen's theorem and thermodynamic availability function.

3. PRELIMINARIES

3.1 System Description

We consider the interconnected system in Fig. 1. Each subsystem \mathcal{M}_k has a conservation law of the form,



Fig. 1. Representation of a network with eight nodes and one zero node in black

$$\mathcal{M}_{k}: \quad \frac{dz_{k}}{dt} = p_{k} + \sum_{i,i \neq k}^{n} q_{ik} \tag{1}$$

In this expression, $z \in \mathbb{R}^n$ denotes the inventory variables, p is the production terms and q_{ik} represents the dedicated flow terms. For each subsystem \mathcal{M}_k we define the potentials

$$w(z)_k = \left(\frac{\partial S}{\partial z}\right)_k \tag{2}$$

where S represents an entropy function. The entropy function is homogenous degree 1, differentiable once and has a unique maximum.

In this work, we are concerned with the process networks as defined in Jillson and Ydstie (2005); Baldea et al. (2013). To illustrate, consider a node with a potential w, convective flow $v = [v_1 \ v_2 \ v_3]^T$ and exchanging heat Qwith the surroundings as shown in Fig. 2. For chemical process systems, the extensive variable z and the intensive variable w are

$$z = \begin{bmatrix} U \\ V \\ N \end{bmatrix}, \quad w = \begin{bmatrix} \frac{1}{T} \\ \frac{1}{T} \\ \frac{1}{T} \\ \frac{-\mu}{T} \end{bmatrix}$$
(3)

This system has the balances for the inventory variables so that



Fig. 2. A single node representing a chemical process in a complex process network

$$\dot{z} = \begin{bmatrix} \sum_{in} v_{in} h_{in} - \sum_{out} v_{out} h_{out} + Q - P \frac{dV}{dt} \\ \Phi + \sum_{in} v_{in} \tilde{v}_{in} - \sum_{out} v_{out} \tilde{v}_{out} \\ r + \sum_{in} v_{in} x_{in} - \sum_{out} v_{out} x_{out} \end{bmatrix}$$
(4)

A crucial step is to define the corresponding flow q_i and production p terms in Eq. 1. We define the flow term q as

$$q = v\tilde{z} + L\Delta w \tag{5}$$

which is the form for the phenomenological relation as in Onsager (1931). In the single node case L = 0, and with $h = u + Pv\tilde{v}$ the dynamics of inventory variables for this node becomes



In Table 1, we provide information on the notation and corresponding physical units.

To further illustrate, we consider the case in which we have two processes interacting with each other as shown in Fig. 3 $\,$



Fig. 3. Two interacting processes

Symbol	Definition	Unit
U	Internal Energy	J
V	Volume	m^3
Ν	number of moles	mol
v	molar flowrate	mol
\tilde{v}	molar volume	<u>m³</u>
Φ	volume change due to mixing/reaction	m^{3}
P	pressure	kPa
T	temperature	С
μ	chemical potential	$\frac{J}{mol}$
h_r	heat of reaction	J
h	molar enthalpy	$\frac{J}{mol}$
u	molar internal energy	$\frac{mpl}{mol}$
r	reaction rate	
x	mole fraction	mol
Q	heat exchange	J
L	symmetric matrix	
w	intensive vector variables	
z	extensive vector variable	
\tilde{z}	molar extensive vector variable	

Table 1. Nomenclature

In this case, the dynamics of the first node, according to Eq. 1, can be described as

$$\frac{dz_1}{dt} = p_1 + q_1 - q_2 \tag{6}$$

$$= p_1 + v_{31}\tilde{z}_3 - \tag{7}$$

$$[v_{12}\tilde{z}_1 - v_{21}\tilde{z}_2 + L_2(w_2 - w_1)] \tag{8}$$

In this situation, $q_1 = v_{31}\tilde{z}_3, q_2 = [v_{12}\tilde{z}_1 - v_{21}\tilde{z}_2 +$ $L_2(w_2 - w_1)$]

It was pointed out by Oster and Desoer (1971) that network representations can be constructed for a wide variety of physical systems. In such a network, the nodes corresponds to the components/units/subsystems and the edges correspond to the interconnections between them. Some examples are; electric circuits, mechanical systems, hydraulic networks, power systems, membranes and in our paper chemical process systems.

Having defined the topology of the network as a directed graph (see Appendix.A) we can use tools (laws of Kirchhoff) originally developed for electric networks to analyse process networks. Given any network topology Kirchhoff laws state:

Lemma 3.1. Kirchhoff's Current Law (KCL): The sum of flows (across variable measurements) identified by the edges in a given network is zero at any instant of time. In a compact form, we have

$$M(G)\mathbf{F} = 0 \tag{9}$$

where M(G) is the incidence matrix as defined in Def. A.4 and **F** is the vector of flows along the edges in the network.

$$\mathbf{F} = [f_1 \ f_2 \ \cdots \ f_e]$$

Lemma 3.2. Kirchhoff's Voltage Law (KVL): The sum of all the potential differences around a loop equals zero

$$\sum \Delta w(z)_{ij} = w(z)_{n_i} - w(z)_{n_j} = 0 \quad \forall \ n \in \mathcal{L}$$

where \mathcal{L} is a loop (see Def. A.7).

We now describe one important theorem known as Tellegen's theorem in electrical network theory. This theorem is later adjusted for process networks of dynamical systems obeying the balance equations (1) and the uniqueness of the potentials (2) that follow from the definition of the entropy function.

Theorem 3.1. Tellegen's Theorem: Consider an arbitrary network with a topology defined by G with n nodes and e edges. Let Δw be any set of potentials satisfying KVL for G and let **F** be any set of flows of satisfying KCL for G. Then:

$$\Delta w^T \mathbf{F} = 0 \tag{10}$$

Proof:

For a directed and connected graph G, let us choose a ground node w_0 . Then, we define an incidence matrix M(G). Since **F** satisfies the balance equation 1 and since for some node-to ground we have

$$M(G)\mathbf{F} = 0\tag{11}$$

Since Δw is unique and for some node-to-ground potentials w_0 , we have

$$\Delta w = M(G)^T \Delta w_0 \tag{12}$$

We can then write

$$(\Delta w)^T \mathbf{F} = (M(G)^T w_0)^T \mathbf{F}$$
(13)

$$=\Delta w_0^T \underbrace{(M(G)^T)^T \mathbf{F}}_{=0}$$
(14)

$$=\Delta w_0^T \mathbf{0} = \mathbf{0} \tag{15}$$

As the potential of the 0-node is assumed to be zero, we can show that the application of Tellegen's theorem to process network gives the following expression. We know that $M^T \mathbf{F} = 0$. This results in conservation laws. Assuming $w_0 = 0$, we have

$$\begin{bmatrix} w_1^T \ w_2^T \ \cdots \ w_n^T \end{bmatrix} \begin{bmatrix} \frac{dz_1}{dt} - p_1 + \sum q_{1j} \\ \frac{dz_2}{dt} - p_2 + \sum q_{2j} \\ \vdots \\ \frac{dz_n}{dt} - p_n - \sum q_{nj} \end{bmatrix} = 0 \quad (16)$$

In this case, we define **F** as

$$\mathbf{F}^{T} = \begin{bmatrix} \frac{dz_{1}^{T}}{dt} & \frac{dz_{2}^{T}}{dt} & \cdots & \frac{dz_{n}^{T}}{dt} & p_{1}^{T} & p_{2}^{T} & \cdots & p_{n}^{T} & q_{12} & q_{13} & \cdots \end{bmatrix}$$
(17)

Expressing the inner product in Equation 16 explicitly, we obtain

$$W_n^T \frac{dZ_n}{dt} = W_n^T P - W_n^T \mathcal{Q}$$
⁽¹⁸⁾

where W_n , Z_n , P_n and Q are the vectors of potentials w_i , extensive variables z_i , production terms p_i and the summation of the flows $\sum q_{ij}$ respectively. We can further express the dynamics of the network including the terminals, as follows.

$$\begin{bmatrix} \frac{dZ_n}{dt} \\ \frac{dZ_t}{dt} \end{bmatrix} = \begin{bmatrix} P_n \\ P_t \end{bmatrix} + \begin{bmatrix} \underline{I_q} \mid 0 \\ 0 \mid I_t \end{bmatrix} \begin{bmatrix} \underline{\mathcal{Q}} \\ T \end{bmatrix}$$
(19)

where T is the vector of flow terms through the terminals, and I is the identity matrix with the corresponding dimensions. The accumulation term $\frac{dZ_t}{dt}$ and the production P_t at the terminals are equal to zero.

Let us define a potential vector for the overall network,

$$W = \left[\begin{array}{c} W_n \\ W_t \end{array} \right]$$

where W_n are the potentials at the nodes and W_t are the potentials at the terminals. Application of Tellegen's theorem 16 both to nodes and terminals results in

$$\begin{bmatrix} W_n^T & W_t^T \end{bmatrix} \frac{d}{dt} \begin{bmatrix} Z_n \\ Z_t \end{bmatrix} = \begin{bmatrix} W_n^T & W_t^T \end{bmatrix} \begin{bmatrix} P_n \\ P_t \end{bmatrix} + \begin{bmatrix} W_n^T & W_t^T \end{bmatrix} \begin{bmatrix} I_q | 0 \\ 0 & |I_t \end{bmatrix} \begin{bmatrix} \mathcal{Q} \\ T \end{bmatrix}$$

The accumulation term and production terms at the terminals are zero. So we get,

$$W_n^T \frac{dZ_n}{dt} = W_n^T P + W_n^T \mathcal{Q} + W_t^T T$$

4. PASSIVITY AND ITS APPLICATION ON THERMODYNAMIC SYSTEMS

A system with states $x \in \mathbb{R}^n$, input $u \in \mathbb{R}^m$ and output $y \in \mathbb{R}^m$ is passive if

$$\int_{0}^{t} u(s)^{T} y(s) ds \ge V(x(t)) - V(x(0))$$
(20)

where V(x(t)) is a storage (Lyapunov) function. In the case of process networks consisting of open multiphase systems, the thermodynamics availability function is proposed and used as a candidate for the storage function V (Alonso and Ydstie, 1996, 1997, 2001)

We define the thermodynamic availability function

$$A(w, z) = (w^*)^T z - S(z)$$
$$= (w^*)^T z - (w)^T z$$
$$= \Delta w^T z$$

where w^* is a fixed reference potential. The availability function represents the distance of a supporting hyperplane tangent to the entropy curve at $z = z^*$ and the entropy $S(z) = w^T z$. It can be used as a Lyapunov function to show stability provided that the appropriate controls are in place. For asymptotic stability, Lyapunov function is required to be strictly positive and the rate of change of this function should be negative. The rate of change of the availability function is derived as

$$\frac{dA}{dt} = -(w - w^*)\frac{dz}{dt} - \frac{dw^T}{dt}z$$

The expression above can be simplified using the Gibbs-Duhem relation $(dw^T)z = 0$, which follows from homogeneity, to

$$\begin{split} \frac{dA}{dt} &= -\Delta w^T \left[\frac{dz}{dt} - \frac{dz^*}{dt} \right] \\ &= -\Delta w^T \frac{d\Delta z}{dt} \end{split}$$

where $\Delta w = (w - w^*)$, $\Delta z = (z - z^*)$ and $\frac{dz^*}{dt} = 0$. Here, the availability function is considered for one process unit. For a network of n processes, the total availability functions is equal to the summation of availability functions of each process.

$$A_{\text{total}} = \sum_{i}^{n} A_{i} = \sum_{i}^{n} \Delta w_{i}^{T} z_{i}$$

The rate of change of total availability can be expressed as

$$\frac{dA_{\text{total}}}{dt} = \sum_{i}^{n} \frac{dA_{i}}{dt} = \sum_{i}^{n} \Delta w_{i}^{T} \frac{\Delta z_{i}}{dt}$$
$$= -\Delta W^{T} \frac{d\Delta Z}{dt}$$

The expression above is actually the difference operator Δ applied to W and $\frac{dZ}{dt}$ in Eq. 18. which is the outcome of the application of Tellegen's theorem on process networks.

$$\frac{dA_{\text{total}}}{dt} = -\Delta W_n^T \Delta P - \Delta W_n^T \Delta Q - \Delta W_t^T T \qquad (21)$$

The next step is to extend the expression in the right hand side and show that $\frac{dA_{total}}{dt}$ is indeed negative provided that the right control actions are in place so that the resulting closed loop system is passive. The properties and the suitability of availability function A for the analysis of stability have been discussed extensively in Ydstie (2018). For multiphase systems, a new Lyapunov function which consists of A and inventories equal to the number of phases should be used.

4.1 The Rate of Change of Availability Function for a Single Unit Process

We consider the single unit as shown in Fig. 4. In the single phase case, we have two terminals (inlet and outlet) and one node denoting the single unit process. Applying



Fig. 4. Single node case

Tellegen's theorem gives

$$w_1^T \frac{dz_1}{dt} = w_1^T p_1 + w_2^T q_{in} - w_3^T q_{out}$$

In this expression, the flow terms are defined so that

$$q_{in} = v_{in}\tilde{z}_2, \quad q_{out} = v_{out}\tilde{z}_3 \tag{22}$$

whereas the production term p_1 takes the form of

$$p_{1} = \begin{bmatrix} (rh_{r})_{1} - P_{1}\frac{dV_{1}}{dt} + Q + v_{in}\tilde{v}_{in}P_{2} - v_{out}\tilde{v}_{out}P_{1} \\ & \Phi_{1} \\ & & r_{1} \end{bmatrix}$$
(23)

Let us express $\Delta w_1^T \Delta \frac{dz}{dt}$ explicitly.

$$\Delta w_1^T \Delta \frac{dz}{dt} = \Delta w_1^T \Delta p_1 + \Delta w_2^T \Delta q_{in} - \Delta w_3^T \Delta q_{out} \quad (24)$$

Extending the right hand side of Eq 24 into its components gives

$$\begin{split} \Delta w_1^T \Delta \frac{dz}{dt} &= -v_{in} \left(\tilde{A} + \tilde{A}^* \right)_{in} + v_{out} \left(\tilde{A} + \tilde{A}^* \right)_{out} \\ &+ \frac{1}{T_1 T_1^*} \Delta P_1 \Delta (T \Phi)_1 + \Delta \left(\frac{P}{T} \right)_{in} \Delta (v \tilde{v})_{in} \\ &- \frac{\Delta P_{in}}{T_{in} T_{in}^*} \Delta (T v \tilde{v})_{in} + \left[\Delta \left(\frac{1}{T} \right)_1 - \Delta \left(\frac{1}{T} \right)_{in} \right] \Delta (P v \tilde{v})_{in} \\ &+ \frac{\Delta P_{out}}{T_{out} T_{out}^*} \Delta (T v \tilde{v})_{out} - \left[\Delta \left(\frac{1}{T} \right)_1 - \Delta \left(\frac{1}{T} \right)_{out} \right] \\ \Delta (P v \tilde{v})_{out} + \Delta \left(\frac{1}{T} \right)_1 \Delta (r h_r)_1 + \Delta \left(\frac{1}{T} \right)_1 \Delta (Q) + \\ \Delta \left(\frac{-\mu}{T} \right)_1 \Delta (r)_1 \end{split}$$

where

$$\tilde{A} = (w^* - w)^T \tilde{z} = -\Delta \left(\frac{1}{T}\right) u - \Delta \left(\frac{P}{T}\right) \tilde{v} + \Delta \left(\frac{\mu}{T}\right)^T x$$
$$\tilde{A}^* = (w - w^*)^T \tilde{z}^* = \Delta \left(\frac{1}{T}\right) u^* + \Delta \left(\frac{P}{T} \tilde{v}^*\right) - \Delta \left(\frac{\mu}{T}\right)^T x^*$$

Due to page limitations we only provide the end result.

Following the same procedure, we can also get an expression for $\frac{-dA_{\text{total}}}{dt}$ for the two phase case in Fig 4 such that

$$\Delta w_1^T \Delta \frac{dz}{dt} = -v_{in} \left(\tilde{A} + \tilde{A}^*\right)_{in} + \sum_{\substack{i=3,4\\j=g,l}} v_i \left(\tilde{A} + \tilde{A}^*\right)_j + \frac{1}{T_1 T_1^*} \Delta P_1 \Delta (T(\Phi^g + \Phi^l)_1 + \Delta \left(\frac{P}{T}\right)_{in} \Delta (v\tilde{v})_{in} - \frac{\Delta P_{in}}{T_{in} T_{in}^*} \Delta (Tv\tilde{v})_{in} + \left[\Delta \left(\frac{1}{T}\right)_1 - \Delta \left(\frac{1}{T}\right)_{in}\right] \Delta (Pv\tilde{v})_{in} + \sum_{\substack{i=3,4\\j=g,l}} \frac{\Delta P_i}{T_i T_i^*} \Delta (T_i v_j \tilde{v}_j) - \sum_{\substack{i=3,4\\j=g,l}} \left[\Delta \left(\frac{1}{T}\right)_1 - \Delta \left(\frac{1}{T}\right)_l\right] \Delta (Pv\tilde{v})_{in} + \Delta \left(\frac{1}{T}\right)_1 \Delta \left((rh_r)_1^g + (rh_r)_1^l\right) + \Delta \left(\frac{1}{T}\right)_1 \Delta (Q) + \Delta \left(\frac{-\mu}{T}\right)_1 \Delta ((r)_1^g + (r)_1^l)$$

In the two phase case, the production term is equal to

$$p_{1} = \begin{bmatrix} (rh_{r})_{1}^{g} + (rh_{r})_{1}^{l} - P_{1}(\Phi_{1}^{g} + \Phi_{1}^{l}) + Q + v_{in}\tilde{v}_{in}P_{2} - \\ \sum_{j=g,l} v_{j}\tilde{v}_{j}P_{1} \\ \Phi_{1}^{g} + \Phi_{1}^{l} \\ r_{1}^{g} + r_{1}^{l} \end{bmatrix}$$
(25)

When we assume that the two phases are at equilibrium, the exchange rates are equivalent and in the opposite direction. This implies $r_1^g = -r_1^l$, $(rh_r)_1^g = -(rh_r)_1^l$, $\Phi_1^g = -\Phi_1^l$. Therefore, the terms with these variables cancel and we get

$$\Delta w_1^T \Delta \frac{dz}{dt} = -v_{in} \left(\tilde{A} + \tilde{A}^*\right)_{in} + \sum_{\substack{i=3,4\\j=g,l}} v_i \left(\tilde{A} + \tilde{A}^*\right)_j$$

$$\frac{1}{T_1 T_1^*} \Delta P_1 \Delta (T(\Phi^g + \Phi^l)_1 + \Delta \left(\frac{P}{T}\right)_{in} \Delta (v\tilde{v})_{in} - \frac{\Delta P_{in}}{T_{in} T_{in}^*} \Delta (Tv\tilde{v})_{in} + \left[\Delta \left(\frac{1}{T}\right)_1 - \Delta \left(\frac{1}{T}\right)_{in}\right] \Delta (Pv\tilde{v})_{in}$$

$$+ \sum_{\substack{i=3,4\\j=g,l}} \frac{\Delta P_i}{T_i T_i^*} \Delta (T_i v_j \tilde{v}_j) - \sum_{\substack{i=3,4\\j=g,l}} \left[\Delta \left(\frac{1}{T}\right)_1 - \Delta \left(\frac{1}{T}\right)_i\right]$$

$$\Delta (P_i v_j \tilde{v}_j) + \Delta \left(\frac{1}{T}\right)_1 \Delta (Q)$$

We have derived expressions of the rate of change of availability function for two specific cases. However, obtaining similar expressions for more general cases like multiple inlet flows and multiple phases is straightforward. For asymptotic stability, the rate of change of the availability function should be negative. By investigating the conditions of asymptotic stability in the expression above, we can find out the type of decentralized control strategy (inout-output pairings) that needs to be used.

5. CONCLUSION AND FUTURE WORK

We have shown that dynamics of extensive variables of a single unit can be obtained by the application of the Tellegen's theorem with the appropriate definitions of the flow variables. Furthermore, availability function has been introduced as a candidate Lyapunov function so that we can design controllers based on passivity. To this end, we derive an expression for the rate of the change of the availability function. This expression has been derived for a single unit with a single phase and binary phases at equilibrium. An initial step forward is the analysis of conditions and control design that leads to a passive system. This work is also going to be extended to several process units with multiple phases and components such as distillation columns, membranes, batteries, fuel cells.

REFERENCES

- Alonso, A. and Ydstie, B. (1996). Process systems, passivity and the second of law of thermodynamics. *Computers and Chemical Engineering*, 20, 1119–1124.
- Alonso, A. and Ydstie, B. (1997). Process systems, passivity via clausius planck inequality. Systems and Control Letters, 30, 253–264.
- Alonso, A. and Ydstie, B. (2001). Stabilization of distributed systems using irreversible thermodynamics. *Automatica*, 37, 1739–1755.
- Baldea, M., El-Farra, N., and Ydstie, B. (2013). Dynamics and control of chemical process networks: Integrating physics, communication and computation. *Computers* and Chemical Engineering, 51, 42–54.

Beya, B. (1998). Modern Graph Theory. Springer.

- Gilles, E.D. (1998). Network theory for chemical processes. Chemical Engineering & Technology, 21(2), 121–132.
- Hangos, K.M., Alonso, A.A., Perkins, J.D., and Ydstie, B.E. (1999). Thermodynamic approach to the structural stability of process plants. *AIChE Journal*, 45(4), 802– 816.

- Jillson, K. and Ydstie, B. (2007). Process networks with decentralized inventory and flow control. *Journal of Process Control*, 17, 399–413.
- Jillson, K. and Ydstie, B.E. (2005). Complex process networks: Passivity and optimality. *IFAC Proceedings Volumes*, 38(1), 543 – 548. 16th IFAC World Congress.
- Kumar, A. and Daoutidis, P. (2002). Nonlinear dynamics and control of process systems with recycle. *Journal of Process Control*, 12(4), 475 – 484.
- Liu, Y.Y., Slotine, J.J., and Barabási, A.L. (2011). Controllability of complex networks. *Nature*, 473, 167–173.
- Mikulecky, D. (2001). Network thermodynamics ann complexity : A transiton to relational system theory. *Computers and Chemistry*, 25, 369–391.
- Onsager, L. (1931). Reciprocal relations in irreversible processes. i. *Phys. Rev.*, 37, 405–426.
- Oster, G.F. and Desoer, C. (1971). Tellegen's theorem and thermodynamic inequalities. *J. Theor. Biol.*
- Oster, G.F. and Perelson, A.S. (1973). Systems, circuits and thermodynamics. *Israel Journal of Chemistry*, 11(2-3), 445–478.
- Oster, G.F. and Perelson, A.S. (1974). Chemical reaction dynamics. Archive for Rational Mechanics and Analysis, 55(3), 230–274.
- Oster, G.F., Perelson, A.S., and Katchalsky, A. (1973). Network thermodynamics: dynamic modelling. *Quarterly Review of Biophysics*, 1, 1–134.
- Penfield, P., Spence, R., and Duinker, S. (1970). Tellegen's theorem and Electric Networks. MIT Press, Cambridge, Massuchusetts.
- Peusner, L. (1981). Premetric thermodynamisc: A topological graphical model. J. Chem. Soc., Farady Trans., 81, 1151–1161.
- Wartmann, M.R. and Ydstie, B.E. (2009). Optimality of process networks. *IFAC Proceedings Volumes*, 42(11), 613–618.
- West, D. (1996). Introduction to Graph Theory. Prentice Hall.
- Ydstie, B.E. (2018). Gibbs's Tangent Plane and Its Application to the Equilibrium Flash. *In preparation*.

Appendix A. DEFINITIONS

Algebraic graph theory is extensively used to represent the topology of networks. We start with the fundamental definitions in the modern graph theory.

Definition A.1. Beya (1998) Consider the set $\mathcal{N}(G) = \{n_1, \cdots, n_k\}$ denoting the set of nodes and the set $\mathcal{E}(G) = \{e_1, \cdots, e_m\}$ the set of edges. A graph G is an ordered pair of disjoint sets $(\mathcal{N}, \mathcal{E})$ such that \mathcal{E} is a subset of the set \mathcal{N} of unordered pairs of \mathcal{N} . k and m represent the number of nodes and the number of edges respectively.

Definition A.2. A directed (oriented) graph G is a pair $(\mathcal{N}, \mathcal{E})$ where \mathcal{N} is a set of nodes and \mathcal{E} is a set of directed edges. If $(n_i, n_j) \in \mathcal{E}$, n_i is known as the source and n_j is the sink of the directed edge \mathcal{E} . An undirected graph has undirected edges.

Definition A.3. A graph G is connected if $\forall (n_i, n_j)$ of distinct vertices, there is a path from n_i to n_j . Otherwise, it is unconnected. An unconnected graph has minimum two separate parts.

Definition A.4. The incidence matrix M(G) of a directed graph G is a $k \times m$ matrix with $M_{i,j} = 1$ if n_i is the tail

of e_j and $M_{i,j} = -1$ if n_i is the head of e_j . If a vertex n belongs to e then n and e are incident.

Definition A.5. Node (vertex) cut of a graph G is a set $S \subseteq \mathcal{N}(G)$ such that S has more than one component. A disconnecting set of edges is a set $\mathcal{F} \subseteq \mathcal{N}(G)$ such that $G - \mathcal{F}$ has more than one component.

Definition A.6. A subgraph of a graph G is a graph H such that $\mathcal{N}(H) \subseteq \mathcal{N}(G)$ and $\mathcal{E}(H) \subseteq \mathcal{E}(G)$

Definition A.7. A loop \mathcal{L} is a subgraph of a graph G such that \mathcal{L} is connected and there are two edges of \mathcal{L} incident with each node.

The information above now helps us to define a general network. The definition is adjusted from West (1996)

Definition A.8. A network is a triplet (G, f) where G is a directed graph with distinguished initial vertices (sources) and distinguished terminal vertices (sinks), and $f : \mathcal{E} \to \mathbb{R}_+$, where f can be capacity of an edge or flow associated with an edge e depending on the problem setting.