

# Passivity of Single-phase Thermodynamic Systems with Equilibrium Reactions<sup>\*</sup>

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**Abstract:** Classical thermodynamics has the standard assumption that there should exist a once differentiable and homogeneous of degree one entropy function with a strict maximum. Based on the concavity assumption, we derive a convex storage function called thermodynamic availability that can be used for passivity-based control design. In this paper, we show that a thermodynamic system with equilibrium reactions controlled by feedback controllers is stable. In particular, the mapping from the feed flow rate to pressure and from the heating/cooling rate to temperature is passive. Simulations of a methane steam reforming reactor provide an example of the control design.

*Keywords:* Equilibrium, Chemical Reaction, Process Control, Stability Analysis, Thermodynamics.

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## 1. INTRODUCTION

The control design of a CSTR with kinetic reactions, for example Arrhenius rate expressions, can be approached by classical methods as studied by Alvarez-Ramirez and Femat (1999); Antonelli and Astolfi (2003). More recently, thermodynamic-based strategies are applied to such problems using the availability function (Hangos et al. (1999); Hoang et al. (2009)) or the Hamiltonian framework (Dorfler et al. (2009)). However, control designs using thermodynamic properties still have many open issues (Hoang et al. (2012)). Despite the obvious importance of reactors operating near the thermodynamic equilibrium, stability theory supporting the control design for such reaction systems with equilibrium constraints is not sufficient. The main problem is that the equilibrium constraints convert the differential system to a differential systems with algebraic constraints, i.e. a DAE system, which makes it difficult to apply classical stability theories, such as Lyapunov's direct and indirect methods.

In this paper, we attempt to explain why low order and well designed PI controllers with feedforward components stabilize chemical process systems with high order and complex nonlinear dynamics. More generally, the theory applies to any controller that is input-strictly passive, such as indirect adaptive controllers, optimal and predictive controllers.

Dissipation of useful work is a consequence of entropy production in irreversible processes. In classical thermodynamics, this is expressed as the maximization of the entropy of an isolated system as postulated by Clausius. In an open system such as a multi-phase distillation process or a chemical reactor, the entropy is no-longer maximized. However, we can still apply the concept of local equilibrium to establish the presence of an equilibrium manifold

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defined by entropy maximization. Along this manifold, we find that the entropy production is minimized and that the inherent irreversibility is quantified by the loss of available work (Salamon and Berry (1983)) or availability as was called by Keenan (1951).

In this paper we use the temperature-scaled availability to define a storage function for passivity-based control. We use the Gibbs equation (Sandler (1999)) to define the entropy, or the primitive surface, as it was called in the first monograph by Gibbs (1906). We furthermore assume that the entropy function has a strict maximum, as postulated by Noll (1970) and show how this leads to the construction of a thermodynamic availability function (Alonso and Ydstie (1996, 2001)) for passivity based control design and stabilization.

## 2. PROBLEM DEFINITION

In this paper we consider the class of positive state space systems that we refer to as *thermodynamic systems*. The state vector  $z$  represents a typical point in the  $n_c + 2$  dimensional space of non-negative reals

$$z = (U, V, N_1, \dots, N_{n_c}) \quad (1)$$

where  $U$  represents the internal energy,  $V$  the volume and  $N_i$  the number of moles of  $i$ -th chemical species, where  $i \in \{1, \dots, n_c\}$ . It follows that  $z$  with elements  $0 \leq z_i < \infty$  define the state space  $\mathbb{Z}$  as an open subset of  $\mathbb{R}_+^{n_c+2}$ .

Components may undergo chemical reactions according to stoichiometric constraints

$$\sum_{i=1}^{n_c} \nu_{i,k} I_i = 0, \quad k = 1, \dots, n_r \quad (2)$$

$I_i$  is chemical formula of species  $i$ ,  $n_r$  is the number of independent chemical reactions, and  $\nu_{i,k}$  is the stoichiometric coefficient of species  $i$  in reaction  $k$ . The stoichiometric coefficients are positive for products, negative for reactants,

and equal to zero for inert species. In addition, we impose equilibrium constraints

$$\sum_{i=1}^{n_c} \nu_{ij} \mu_i(z) = 0, \quad j = 1, \dots, n_r \quad (3)$$

where  $\mu_i(z)$  is the chemical potential of the  $i$ th species. The justification of equation 3 is provided in appendix A.

Such systems have non-negative states and dynamics constrained so that they satisfy the second law of thermodynamics. Specifically, the dynamics satisfy the conservation laws

$$\frac{dz}{dt} = \phi(z, u, d), \quad z(0) \text{ given} \quad (4)$$

The state variables are non-negative with  $z(0)$  being the initial condition. The function  $\phi(z, u, d)$  depends on the state, and vectors  $u$  and  $d$  of controls and disturbances.

An output vector

$$y = h(z) \quad (5)$$

is defined to model measured outputs.

The problem addresses how to choose the vector of control variables  $u$  and output variables  $y$  so that the mapping  $u \mapsto y$  defined by the equilibrium constrained system (4 - 5) is passive. I.e. that there exists a positive definite storage function  $W(z)$  so that

$$\frac{dW(z)}{dt} \leq u^T y$$

for all valid disturbance signals. In addition we need to establish the existence, stability and uniqueness of the solutions to the differential equations (4) with algebraic constraints (3) when we apply passivity based controls of the type  $u = C(y)$  where  $C(\cdot)$  is output strictly passive.

### 3. THERMODYNAMIC SYSTEMS

Classical thermodynamics is based on the idea that a nonlinear function of the state, called the entropy, achieves its maximum at equilibrium.

We claim the following properties

The entropy function  $S: \mathbb{Z} \rightarrow \bar{\mathbb{R}}_+$  is differentiable at least once. Furthermore

- (1) The entropy is homogeneous degree one, i.e.  $S(\lambda z) = \lambda S(z)$ .
- (2) The temperature is positive, i.e.  $T = \partial U / \partial S > 0$ , and  $S(z) \rightarrow 0$  as  $T \rightarrow 0$ .
- (3) The entropy has a strict maximum for isolated systems.

The Euler equation gives the important relation

$$S(z) = w^T z \quad (6)$$

where  $w$  is a vector of intensive variables defined by

$$\begin{aligned} w &= \nabla S(z) \\ &= \left( \frac{\partial S}{\partial U}, \frac{\partial S}{\partial V}, \frac{\partial S}{\partial N_1}, \dots, \frac{\partial S}{\partial N_{n_c}} \right) \\ &= \left( \frac{1}{T}, \frac{P}{T}, -\frac{\mu_1}{T}, \dots, -\frac{\mu_{n_c}}{T} \right) \end{aligned} \quad (7)$$

Application of these properties establishes the phase rule,  $n_f = n_c + 2 - n_p - n_r$ . It establishes the rank of the mapping  $w(z) = \nabla S$  at the point  $z$ . Due to homogeneity,

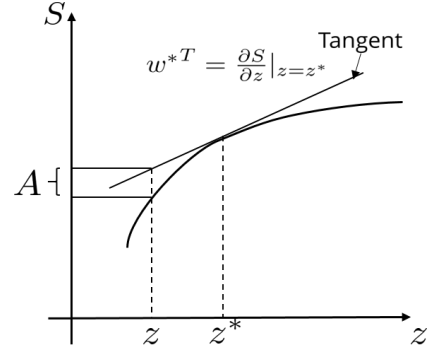


Fig. 1. Thermodynamic availability and the entropy functions with respect to the state space  $z$

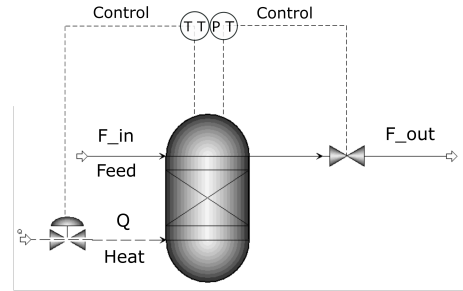


Fig. 2. A illustrative example of a gas-phase reactor with heat and outward flow control

its rank is always less than  $n_c + 2$ . Strict maximality ensures that the phase distribution is unique<sup>1</sup>.

The concavity of entropy makes it a good candidate to define a storage function for passivity-based design of feedback control systems. By taking the difference between the supporting hyperplane  $z^T w(z^*)$  at a given point  $z^*$  and the entropy function at  $z$ , we define a distance function

$$A(z, z^*) = z^T w^* - S(z) \quad (8)$$

where  $w^* = \nabla S(z)|_{z=z^*}$ . The concavity of the entropy  $S$  guarantees that the availability (8) is positive definite<sup>2</sup>. An illustrative example of a homogeneous thermodynamic system is shown in Fig 1.

### 4. PASSIVITY BASED CONTROL OF GAS-PHASE EQUILIBRIUM REACTORS

In this section, a passivity-based control design is developed for the single phase reactive system shown in Fig 2 based on thermodynamic notations introduced in section 3. The internal energy, volume, and component balances are given by

<sup>1</sup> The assumption of strict maximization can be replaced by genericity (nothing is really flat), by second order differentiability and with it strict local concavity at the equilibrium phase distribution, or equivalently, the validity of the phase rule.

<sup>2</sup> The availability is related to the Exergy and also to the Bregman distance (Bregman (1967)). The main difference with Bregman being that  $A$  is homogeneous degree one and not positive definite in  $z$ . However, it follows from the phase rule that it is positive definite in  $w(z)$

$$\begin{aligned}
\frac{dU}{dt} &= \hat{H}^{in} F^{in} - \hat{H}^{out} F^{out} + Q \\
\frac{dV}{dt} &= 0 \\
\frac{dN_i}{dt} &= F^{in} x_i^{in} - F^{out} x_i^{out} + p_i(U, V, N_1, \dots, N_{n_c})
\end{aligned} \tag{9}$$

$F$  represents molar flow rates,  $\hat{H}$  is a compact notation for the molar enthalpies and  $x_i$  represents the mole fraction of species  $i$  in a flow. The subscripts “in” and “out” denote flows into and out of the reactor.  $p_i$  represents the production term due to chemical reactions for species  $i$ .  $Q$  denotes the rate of heat transfer to the reactor.

**Lemma 1. Availability for the single phase reactor**  
Consider the thermal system (9) with equilibrium constraints (3). The availability function then satisfies

$$\frac{dA}{dt} = d^{in} - d^{out} + s^{in} - \frac{\Delta P}{TT^*} \Delta(F\hat{T}\hat{v})^{out} + \frac{1}{TT^*} \Delta T \Delta Q$$

with dissipation

$$\begin{aligned}
d^{in} &= -(\omega - \omega^*)^T (F\hat{z} - (F\hat{z})^*)^{in} \\
d^{out} &= -(\omega - \omega^*)^T (F\hat{z} - (F\hat{z})^*)^{out}
\end{aligned}$$

where  $\hat{z}$  are molar quantities of  $z$  and

$$s^{in} = -\Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{in} + \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{in}$$

**Proof.** From equation (8), the time derivative of the available function can be written as

$$\frac{dA}{dt} = w^*{}^T \frac{dz}{dt} - \frac{dS_D}{dt} \tag{10}$$

Homogeneity gives  $\frac{dS_D}{dt} = w^T \frac{dz}{dt}$ , we then get

$$\frac{dA}{dt} = w^*{}^T \frac{dz}{dt} - w^T \frac{dz}{dt}$$

To simplify the notation, the deviation operator  $\Delta$  is introduced so that

$$\Delta w = w - w^* \quad \Delta z = z - z^*$$

The reference state is time invariant so that

$$\frac{d\Delta z}{dt} = \frac{dz}{dt}$$

Now the time derivative of the availability function has the form

$$\frac{dA}{dt} = -\Delta w^*{}^T \frac{d\Delta z}{dt} \tag{11}$$

Expanding the right hand side into the product of each component of  $\Delta z$  and  $\Delta w$  using equations (9) and (7)

$$\begin{aligned}
\frac{dA}{dt} &= -\Delta\left(\frac{1}{T}\right)\frac{d\Delta U}{dt} - \Delta\left(\frac{P}{T}\right) \cdot 0 + \Delta\left(\frac{\mu}{T}\right)^T \frac{d\Delta N}{dt} \\
&= -\Delta\left(\frac{1}{T}\right)\Delta((F\hat{H})^{in} - (F\hat{H})^{out} + Q) \\
&\quad + \sum_{i=1}^{n_c} \Delta\left(\frac{\mu_i}{T}\right)^T \Delta((x_i F)^{in} - (x_i F)^{out} + p_i)
\end{aligned}$$

According to the definition of molar enthalpy  $\hat{H} = \hat{U} + P\hat{V}$ , where  $\hat{U}$  is the molar internal energy,  $P$  is the pressure, and  $\hat{V}$  represents the molar volume, now

$$\begin{aligned}
\frac{dA}{dt} &= -\Delta\left(\frac{1}{T}\right)\Delta(F\hat{U})^{in} - \Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{in} \\
&\quad + \Delta\left(\frac{1}{T}\right)\Delta(F\hat{U})^{out} + \Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{out} \\
&\quad - \Delta\left(\frac{1}{T}\right)\Delta Q \\
&\quad + \sum_{i=1}^{n_c} \left( \Delta\left(\frac{\mu_i}{T}\right)^T \Delta(x_i F)^{in} - \Delta\left(\frac{\mu_i}{T}\right)^T \Delta(x_i F)^{out} \right) \\
&\quad + \sum_{i=1}^{n_c} \Delta\left(\frac{\mu_i}{T}\right)^T \Delta p_i
\end{aligned}$$

For species  $i$ ,

$$p_i = \sum_{j=1}^{n_R} \nu_{ij} \epsilon_j$$

where  $\epsilon_j$  is the rate of the  $j$ th reaction.

$$\begin{aligned}
\Delta\left(\frac{\mu_i}{T}\right)\Delta p_i &= \Delta\left(\frac{\mu_i}{T}\right)\Delta \sum_{j=1}^{n_R} \nu_{ij} \epsilon_j \\
&= \Delta\left(\frac{\mu_i}{T}\right) \sum_{j=1}^{n_R} \nu_{ij} \Delta \epsilon_j \\
&= \frac{1}{T} \sum_{j=1}^{n_R} \mu_i \nu_{ij} \Delta \epsilon_j - \frac{1}{T^*} \sum_{j=1}^{n_R} \mu_i^* \nu_{ij} \Delta \epsilon_j
\end{aligned}$$

Considering all species

$$\begin{aligned}
&\sum_{i=1}^{n_c} \Delta\left(\frac{\mu_i}{T}\right)\Delta p_i \\
&= \frac{1}{T} \sum_{i=1}^{n_c} \sum_{j=1}^{n_R} \mu_i \nu_{ij} \Delta \epsilon_j - \frac{1}{T^*} \sum_{i=1}^{n_c} \sum_{j=1}^{n_R} \mu_i^* \nu_{ij} \Delta \epsilon_j \\
&= \frac{1}{T} \sum_{j=1}^{n_R} \Delta \epsilon_j \sum_{i=1}^{n_c} \mu_i \nu_{ij} - \frac{1}{T^*} \sum_{j=1}^{n_R} \Delta \epsilon_j \sum_{i=1}^{n_c} \mu_i^* \nu_{ij}
\end{aligned}$$

For single-phase systems reaching reaction equilibrium, the production term  $p$  is shown to be 0 using the equilibrium criterion, the proof of which is in Appendix A. The equilibrium criterion gives

$$\sum_{i=1}^{n_c} \mu_i \nu_{ij} = 0 \quad \sum_{i=1}^{n_c} \mu_i^* \nu_{ij} = 0$$

Hence

$$\sum_{i=1}^{n_c} \Delta\left(\frac{\mu_i}{T}\right)\Delta p_i = 0$$

$$\begin{aligned} \frac{dA}{dt} = & \\ & - \Delta\left(\frac{1}{T}\right)\Delta(F\hat{U})^{in} - \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{in} + \Delta\left(\frac{\mu}{T}\right)^T \Delta(xF)^{in} \end{aligned} \quad (12)$$

$$+ \Delta\left(\frac{1}{T}\right)\Delta(F\hat{U})^{out} + \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{out} - \Delta\left(\frac{\mu}{T}\right)^T \Delta(xF)^{out} \quad (13)$$

$$- \Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{in} + \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{in} \quad (14)$$

$$+ \Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{out} - \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{out} \quad (15)$$

$$- \Delta\left(\frac{1}{T}\right)\Delta Q \quad (16)$$

Applying the well-mixed assumption, we expand and re-arrange terms in expression (15)

$$\begin{aligned} & - \Delta\left(\frac{1}{T}\right)\Delta(FP\hat{V})^{out} + \Delta\left(\frac{P}{T}\right)\Delta(F\hat{V})^{out} \\ = & \frac{1}{TT^*}(T - T^*)(FP\hat{V} - (FP\hat{V})^*)^{out} \\ & + \frac{1}{TT^*}(PT^* - P^*T)(F\hat{V} - (F\hat{V})^*)^{out} \\ = & \frac{1}{TT^*}(PTF\hat{V} - P^*TF\hat{V} - P(TF\hat{V})^* + (PTF\hat{V})^*)^{out} \\ = & \frac{1}{TT^*}\Delta P\Delta(TF\hat{V})^{out} \end{aligned}$$

We use  $s^{in}$  to define expression (14) as is stated in lemma 1.

For equation 16,

$$- \Delta\left(\frac{1}{T}\right)\Delta Q = \frac{\Delta T}{TT^*}\Delta Q$$

Combining derived terms together gives the proposed expression in lemma 1.

For a gas-phase equilibrium reactor with fixed feed conditions:

- the deviation in feed conditions equals zero, i.e.  $d^{in}$  with expression 12 and  $s^{in}$  is zero, according to the assumption of fixed feed conditions.
- $d^{out} = -(\omega - \omega^*)^T (F\hat{z} - F\hat{z}^*)^{out} = F^{out}(C_1 A(z, z^*) + C_2 A(z^*, z)) \geq 0$ , where  $C_1$  and  $C_2$  are positive numbers scaled by mole numbers.

Lemma 1 shows that a single-phase equilibrium reactor with fixed feed conditions is strictly passive with

$$u = \Delta\left(\frac{F\hat{V}^{out}}{Q}\right), \quad y = \Delta\left(\frac{P}{T}\right) \quad (17)$$

where  $F\hat{V}^{out}$  is the volumetric out flow.

## 5. METHANE STEAM REFORMING

The steam reforming reaction accounts for up to 95% of the world's hydrogen production and most ammonia is produced by the Haber Bosch process. Both processes and many other industrial examples such as the production of sulfuric acid and lime are governed by chemical equilibrium. In this section, a methane steam reforming reactor with control design shown in equation (17) is modeled in MATLAB.

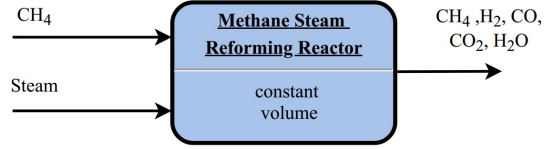
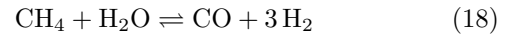


Fig. 3. Model Example: Water gas shift reactor with constant volume

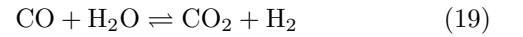
The materials flowing in and out of the reactor is shown in Fig 3 The system is simplified by applying the following assumptions:

- The reactor operates as a CSTR and all components are in gas phase.
- The gases are treated as ideal.
- The kinetics at high temperatures are fast so that the chemical equilibrium is reached by Minimizing Gibbs free Energy.

Methane reacts with water to produce syn-gas ( $\text{CO} + \text{H}_2$ ).



Carbon monoxide and water undergo water gas shift reaction to form hydrogen and carbon dioxide.



### 5.1 Reaction Invariants and Thermodynamic Mapping

Elements are conserved during chemical reactions and are referred to as reaction invariants. Under the assumption of reaction equilibrium, the invariant space  $z_I$  can be mapped into the component space  $z_C$  by applying thermodynamic data of the system.

$$\underbrace{\begin{pmatrix} P \\ T \\ N_C \\ N_H \\ N_O \end{pmatrix}}_{\text{invariant space}} \xrightarrow[\text{mapping}]{\text{thermodynamic}} \underbrace{\begin{pmatrix} U \\ V \\ N_{\text{CO}_2} \\ N_{\text{CO}} \\ N_{\text{H}_2} \\ N_{\text{H}_2\text{O}} \\ N_{\text{CH}_4} \end{pmatrix}}_{\text{component space}}$$

Under the assumption of reaction equilibrium, the minimization of Gibbs free energy is a good candidate for the thermodynamic mapping. The algorithm can be considered as a constrained optimization problem under given temperature and pressure in the following form

$$\begin{aligned} \min \quad & G = \sum_{j=1}^5 \mu_j(N_j)N_j \\ \text{s.t.} \quad & N_C = N_{\text{CO}} + N_{\text{CO}_2} + N_{\text{CH}_4} \\ & N_H = 2N_{\text{H}_2} + 2N_{\text{H}_2\text{O}} + 4N_{\text{CH}_4} \\ & N_O = N_{\text{CO}} + 2N_{\text{CO}_2} + N_{\text{H}_2\text{O}} \end{aligned} \quad (20)$$

The minimum is unique due to strict maximization in the entropy formulation.

### 5.2 Modeling Framework

The general equations for a system model based on reaction invariants have the following form

$$\begin{aligned}\frac{dz_I}{dt} &= \phi(x, d, u) \\ x &= h(z_I)\end{aligned}\quad (21)$$

where  $z_I$  represents the reaction invariants. The equation  $x = h(z_I)$  is the thermodynamic mapping function that maps the invariant state space to the equilibrium component state space. If a process system under equilibrium is modeled in a framework based on reaction invariants, the mass balance described by reaction invariants is a set of first-order linear differential equations as the net change depend only on boundary flows. The higher order terms including production and consumption of components are considered in the equilibrium thermodynamic calculation.

For the water gas shift model, there are two separate inlets for steam and methane and one single outlet for reaction products. The inlet molar flow rates are fixed. Based on lemma 1, the system is passive with respect to the input-output pairs shown in 17 and the can be stabilized by simple feedback controllers. The outlet molar flow rate is controlled by a PI controller to achieve a desired pressure set point.

$$\begin{aligned}F^{out}(t) &= k_p \left( e_P(t) + \frac{1}{T_i} \int_0^t e_P(\tau) d\tau \right) \\ e_P(t) &= P(t) - P^*(t)\end{aligned}$$

The energy balance is written as

$$\frac{dU}{dt} = \hat{H}^{in} F^{in} - \hat{H}^{out} F^{out} + Q \quad (22)$$

where  $\hat{H}_{in}$  and  $\hat{H}_{out}$  are molar enthalpies of formation of components in the inlet and outlet flows respectively and  $F_{in}$  and  $F_{out}$  are molar flow rates.  $Q$  represents the rate of heat transfer to the system. We first derive the time derivative of temperature from the energy balance. Expand the expression of the internal energy on the left-hand side of equation 22, we get

$$U = \sum_{j=1}^5 N_j u_j \quad (23)$$

and

$$\frac{dU}{dt} = \sum_{j=1}^5 u_j \frac{dN_j}{dt} + \sum_{j=1}^5 N_j \frac{du_j}{dt} \quad (24)$$

Applying the assumptions of reaction equilibrium and ideal gas mixture, we have

$$\frac{dU}{dt} = \sum_{j=1}^5 N_j \frac{du_j}{dt} = \sum_{j=1}^5 N_j c_{v,j} \frac{dT}{dt} \quad (25)$$

where  $C_{v,j}$  is the molar heat capacity at constant volume and  $u_j$  is the molar internal energy of species  $j$ .

In order to control the temperature of the system to a set point, a PI controller is implemented in the heat supply such that

$$\begin{aligned}Q &= k_p \left( e_T(t) + \frac{1}{T_i} \int_0^t e_T(\tau) d\tau \right) - \hat{H}^{in} F^{in} + \hat{H}^{out} F^{out} \\ e_T(t) &= T(t) - T^*(t)\end{aligned}$$

The closed-loop system of the water gas shift tank with reaction invariants is written as

$$\begin{aligned}\frac{dN_C}{dt} &= F_{CH_4}^{in} - F^{out}(x_{CO_2} + x_{CO} + x_{CH_4}) \\ \frac{dN_H}{dt} &= 4F_{CH_4}^{in} + 2F_{H_2O}^{in} - F^{out}(2x_{H_2} + 2x_{H_2O} + 4x_{CH_4}) \\ \frac{dN_O}{dt} &= F_{H_2O}^{in} - F^{out}(2x_{CO_2} + x_{CO} + x_{H_2O}) \\ \frac{dT}{dt} &= k_p \left( e_P(t) + \frac{1}{T_i} \int_0^t e_P(\tau) d\tau \right) / \left( \sum_{j=1}^5 N_j c_p(N_j, T) \right) \\ \begin{pmatrix} U \\ V \\ N_J \end{pmatrix} &= h \begin{pmatrix} P \\ T \\ N_I \end{pmatrix} \\ F^{out}(t) &= k_p \left( e_P(t) + \frac{1}{T_i} \int_0^t e_P(\tau) d\tau \right)\end{aligned}$$

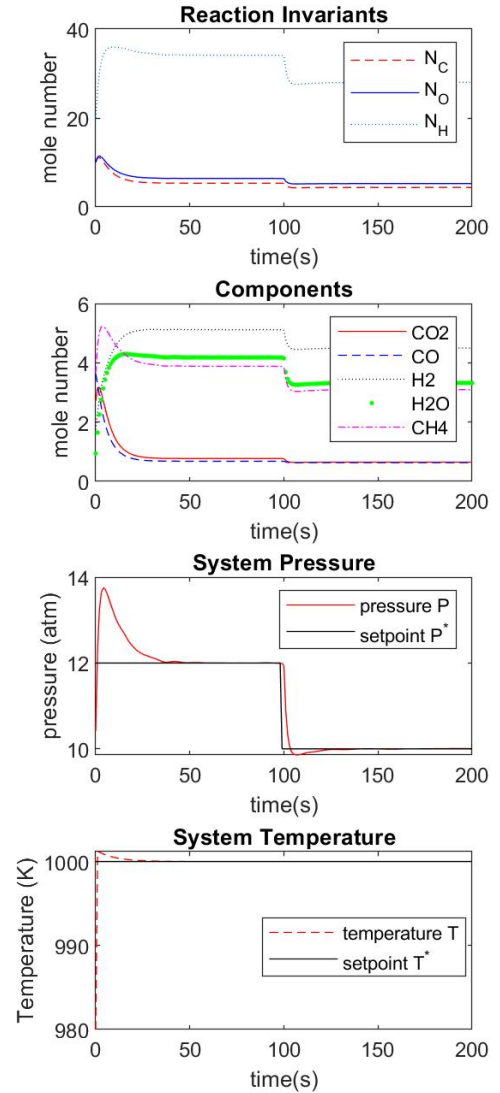


Fig. 4. Example of Pressure set point change for the water gas shift reactor model

$N_J$  is a compact notation for mole numbers of chemical species and  $N_I$  is a compact notation for mole numbers of atoms. The DAE system above has index 1 and is solved by MATLAB solver `ode15s` and the thermodynamic mapping is solved by nonlinear programming solver `fmincon`. In this case, the Gibbs minimization problem has a unique solution so a global solver is not needed.

The following simulation example illustrates the application of the theory to the water gas shift reactor model and its control system. The result is shown in figure 4. Given a constant volume gas phase system, the molar flow rates of methane and steam are fixed. The temperature set point is 1000K and the system is able to reach a new state of equilibrium after a step change in the set point of pressure.

## 6. CONCLUSION

Passivity-based control theory is applied to the stability analysis of a gas-phase equilibrium reactor with fixed feed conditions. A thermodynamic availability function is developed as the storage function, which leads to feedback control design of the reactor system. It can be shown that the pressure and temperature of a gas-phase equilibrium reactor can be stabilized with feedback controls of outward flow and heat supply respectively. The theorem developed in this paper is applicable to reaction systems with more complex dynamics. For future studies, stability analysis of a multi-phase equilibrium reactor is considered. Chemical reactors described by PDE systems with varied feed conditions and spatial discretization of temperature and material concentration is also a promising direction.

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## Appendix A. THE EQUILIBRIUM CRITERION

For a single chemical reaction, the molar extent of reaction  $X$  is related to mole number  $N_i$  of a specie  $i$  in the reaction at any time  $t$  and the initial mole number  $N_{i,0}$  by the following equation

$$N_i = N_{i,0} + \nu_i X \quad (\text{A.1})$$

$X$  is defined in a way such that it is the same for every chemical species in a single reaction. Considering a closed single-phase constant temperature and constant pressure system with multiple chemical reactions, the mole number of species  $i$  at any time is

$$N_i = N_{i,0} + \sum_{j=1}^{n_R} \nu_{ij} X_j \quad (\text{A.2})$$

The total Gibbs free energy energy of the system can be written as

$$\begin{aligned} G &= \sum_{i=1}^{n_c} N_i \mu_i = \sum_{i=1}^{n_c} \left( N_{i,0} + \sum_{j=1}^{n_R} \nu_{ij} X_j \right) \mu_i \\ &= \sum_{i=1}^{n_c} N_{i,0} \mu_i + \sum_{i=1}^{n_c} \sum_{j=1}^{n_R} \nu_{ij} X_j \mu_i \end{aligned} \quad (\text{A.3})$$

At chemical equilibrium, the Gibbs free energy is minimized and partial derivation of  $G$  with respect to all reaction variables are zero. For the system of interest, this gives

$$\left( \frac{\partial G}{\partial X_j} \right)_{T,P,X_{i \neq j}} = 0 \quad j = 1, 2, \dots, n_R \quad (\text{A.4})$$

and then for all reactions  $j = 1, 2, \dots, n_R$

$$\sum_{i=1}^{n_c} N_{i,0} \left( \frac{\partial \mu_i}{\partial X_j} \right)_{T,P,X_{i \neq j}} + \sum_{i=1}^{n_c} \nu_{ij} \mu_i = 0 \quad (\text{A.5})$$

The generalized Gibbs-Duhem equation gives

$$\sum_{i=1}^{n_c} N_{i,0} \left( \frac{\partial \mu_i}{\partial X_j} \right)_{T,P,X_{i \neq j}} = 0 \quad (\text{A.6})$$

Combining equation A.5 and equation A.6 gives

$$\sum_{i=1}^{n_c} \nu_{ij} \mu_i = 0 \quad (\text{A.7})$$