

# A thermodynamic approach towards Lyapunov based control of reaction rate

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**Abstract:** This paper proposes a Lyapunov-based approach for the control of reaction rate involved in chemical reactors through the use of irreversible thermodynamics. More precisely, the reaction rate is structurally derived as a nonlinear function of the reaction force in order to ensure the inherent non-negative definiteness property of the irreversible entropy production due to the reaction. On this basis, it allows to cover a large class of reaction rates described by the mass-action-law. As a consequence, the control of the reaction rate consists in controlling the reaction force through the support of an affinity-related storage function to operate the entire system at a desired operating point. Besides, the convergence condition is given.

*Keywords:* Lyapunov function, thermodynamics, affinity, entropy production, CSTR.

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## 1. INTRODUCTION

A number of control strategies have been proposed to deal with the nonlinear feedback control of homogeneous chemical reactors, and in particular of unstable continuous stirred tank reactors (CSTRs). Several applications of nonlinear control methods to CSTRs can be found in a large number of references, e.g. nonlinear feedback control under constraints (Viel *et al.* (1997); Bayer *et al.* (2011); Hoang & Dochain (2013d)), Lyapunov-based control (Antonelli & Astolfi (2003)), nonlinear PI control (Alvarez-Ramírez & Morales (2000)), port (pseudo) Hamiltonian framework (Hudon *et al.* (2008); Hangos *et al.* (2001); Dörfler *et al.* (2009); Hoang *et al.* (2011); Ramírez *et al.* (2013)), power/energy-shaping control (Favache & Dochain (2010); Alvarez *et al.* (2011)) and inventory control (Farschman *et al.* (1998); Hoang *et al.* (2013e)).

As shown in the works of (Georgakis (1986); Favache & Dochain (2009)), the reaction kinetics plays a central role as the source generating the abnormal dynamical behavior of the reaction system (for example, multiple steady states or non-minimum phase behaviors (Hoang *et al.* (2013c))) through the influence of its inherently nonlinear characteristics. In that respect, the results presented in (Dammers & Tels (1974); Tarbell (1977); Ydstie & Alonso (1997); Eberard *et al.* (2007); Ederer *et al.* (2011); Hoang *et al.* (2012); Hoang & Dochain (2013a,b)) were dedicated to an active research area where the use of thermodynamics for the stability analysis and control design of chemical reaction networks is considered.

This paper deals with the nonlinear control of the unstable CSTR via controlled reaction rate in the context of

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thermodynamics together with Lyapunov-based approach. More precisely, the objective of this paper is to explore some previous results given in (Couenne *et al.* (2006); Favache & Dochain (2009); Hoang *et al.* (2011)) in order to characterize more precisely the dynamics of the CSTR which is inherently associated with the irreversibility property along all dynamical trajectories. On this basis, it allows to propose a structured representation of the reaction rate as a nonlinear function of the reaction force involved in the reaction course in order to guarantee the sign constraint of the irreversibility (such as the non-negative entropy production (Hoang & Dochain (2013a))). Consequently, the stabilization of the reaction rate is equivalently treated by controlling the reaction force to operate the overall system at a desired operating point.

The paper is organized as follows. Section 2 presents the CSTR model, some thermodynamic concepts and instrumental properties required for the present work. The irreversible entropy production due to the reaction as well as its non-negative property is considered in Section 3. This property is central to derive a structured representation of the reaction rate through the use of conjugated reaction force. Section 4 proposes a candidate Lyapunov function usable for the stabilization of the unstable CSTR via controlled reaction rate. An example is included to illustrate the proposed developments.

## 2. THERMODYNAMICS AND ITS USE FOR MODELING OF THE CSTR

### 2.1 A general view of the CSTR model

Let us consider a liquid phase CSTR under isobaric conditions with one reversible reaction involving 2 species  $A$  and  $B$  (Hoang *et al.* (2011)) :

$$\nu_A A \frac{r_f}{r_r} \nu_B B \quad (1)$$

where  $\nu_A$  and  $\nu_B$  are the stoichiometric coefficients. Note also that the net reaction rate  $r$  of the reaction (1) can also be expressed as follows :

$$r = r_f - r_r \quad (2)$$

where  $r_f$  and  $r_r$  are the forward and reverse reaction rates, respectively. In that respect, this necessarily implies that  $\nu_A < 0$  and  $\nu_B > 0$  (Ramírez *et al.* (2013)).

Let us consider the following modeling assumptions (Hoang & Dochain (2013a)) :

**(H1)** The fluid mixture is ideal and incompressible.

**(H2)** The reactor is fed by the species  $A$  and  $B$  through the inlet molar flow rates  $F_{AI}$  and  $F_{BI}$ , respectively at a fixed temperature  $T_I$ .

**(H3)** The reaction rate  $r$  depends only on the temperature of the reaction mixture, and on the concentrations of the involved species. The net reaction  $r > 0$  is such that the species  $A$  is consumed, whereas  $r < 0$  if the species  $A$  is produced. The case  $r = 0$  corresponds to the chemical equilibrium. Furthermore, the reaction rate  $r$  fulfills thermodynamic constraints as follows (Sandler (1999); Favache & Dochain (2010); Alvarez *et al.* (2011)) :

$$\lim_{T \rightarrow 0} r = 0 \quad \text{and} \quad \lim_{T \rightarrow +\infty} r = r_{\max} \quad (3)$$

**Notation:** Let  $\mathcal{I} = \{A, B\}$  denote the set of chemical species involved in the reaction mixture (1).

## 2.2 Thermodynamically consistent CSTR modeling

The continuous stirred tank reactors (CSTRs) belong to a large class of open thermodynamic systems with mass and/or energy exchanges with the surrounding environment. The system variables can be split into an extensive variables vector  $Z$  (composed of the enthalpy  $H$  and the molar numbers  $N_i$ ,  $\forall i \in \mathcal{I}$ ) and an intensive variables vector  $w$  (such as the temperature  $T$  and the chemical potentials  $\mu_i$ ,  $\forall i \in \mathcal{I}$ ). The difference between the extensive and intensive quantities lies in the fact that the extensive quantity depends on the volume of the system. Let us write those vectors in a compact form with the entropy representation (Callen (1985)) :

$$Z = (N_A, N_B, H)^T \quad \text{and} \quad w = \left( \frac{-\mu_A}{T}, \frac{-\mu_B}{T}, \frac{1}{T} \right)^T \quad (4)$$

The system dynamics is given by considering the material and energy balance equations on the basis of the extensive variables vector  $Z$  (4) (Favache & Dochain (2010); Hoang *et al.* (2012)) :

$$\frac{dN_A}{dt} = F_{AI} - F_A + \nu_A r V \quad (5)$$

$$\frac{dN_B}{dt} = F_{BI} - F_B + \nu_B r V \quad (6)$$

$$\frac{dH}{dt} = \dot{Q}_J + \sum_{i \in \mathcal{I}} (F_{iI} h_{iI} - F_i h_i) \quad (7)$$

where  $(F_A, F_B)^T$ ,  $(h_{AI}, h_{BI})^T$ ,  $(h_A, h_B)^T$  and  $\dot{Q}_J$  are the outlet flow rate vector, the inlet and outlet molar enthalpy

vectors and the heat flow rate coming from the jacket, respectively. The volume of the CSTR is denoted by  $V$ .

*Remark 1.* In equilibrium thermodynamics, the variation of the entropy  $S$  is given by considering the Gibbs' equation (Callen (1985)) :

$$dS = w^T dZ \quad (8)$$

Consequently,

$$w(Z)^T = \frac{\partial S(Z)}{\partial Z} \quad (9)$$

As the entropy  $S$  is also an extensive variable, it is thus an homogeneous function of degree 1 with respect to  $Z^2$ . We get by using the Euler's theorem (Callen (1985)) :

$$S(Z) = w^T Z \quad (10)$$

This implies that  $w(Z)$  (9) is a homogeneous function of degree 0 with respect to  $Z$ .

Let us complete the system dynamics representation by the entropy balance on the basis of the second law of thermodynamics (see also (Couenne *et al.* (2006); Favache & Dochain (2009); Hoang *et al.* (2011))) :

$$\frac{dS}{dt} = \Phi_s + \Sigma_s \quad \text{and} \quad \Sigma_s \geq 0 \quad (11)$$

where :

$$\Phi_s = \sum_{i \in \mathcal{I}} (F_{iI} s_{iI} - F_i s_i) + \frac{\dot{Q}_J}{T} \quad (12)$$

$$\begin{aligned} \Sigma_s = & \sum_{i \in \mathcal{I}} \frac{F_{iI}}{T} (h_{iI} - T s_{iI} - \mu_i) \\ & + \left( \frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \right) + \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} r V \geq 0 \end{aligned} \quad (13)$$

with  $\Phi_s$  and  $\Sigma_s$  the entropy exchange flow rate with surrounding environment (due to convection and thermal exchange) and the irreversible entropy production, respectively. The source term  $\Sigma_s$  is always non-negative along the system dynamics (5)-(7) in accordance to the second law of thermodynamics (De Groot & Mazur (1962)).

*Remark 2.* The non-negative property of the entropy production  $\Sigma_s$  (13) represents the so-called irreversibility degree of the system dynamics. Its transcription in terms of Lyapunov stability theory (Khalil (2002)) for the control design of open reaction systems is not obvious because the negative definiteness condition on the entropy production variation has only been emphasized with linear phenomenological laws provided by the Onsager symmetric relations (De Groot & Mazur (1962); Tarbell (1977); Ydstie & Alonso (1997)). Let us note that the non isothermal CSTR is a special but important case of open reaction systems where nonlinear phenomenological laws, and in particular, nonlinear reaction kinetics are considered (Favache & Dochain (2009)).

*Remark 3.* The partial molar enthalpy and entropy of the chemical species  $i$ ,  $\forall i \in \mathcal{I}$  within an ideal isobaric mixture are given by the following expressions (Sandler (1999)) :

<sup>2</sup> Let  $f : \mathcal{R}^n \rightarrow \mathcal{R}$ , the function  $f$  is said to be homogenous of degree  $k$  if  $\forall x \in \mathcal{R}^n$  and  $\gamma \in \mathcal{R}^{*+}$ ,  $f(\gamma x) = \gamma^k f(x)$ .

$$h_i(T, x_i) = c_{pi}(T - T_{ref}) + h_{i,ref} \quad (14)$$

$$s_i(T, x_i) = c_{pi} \ln\left(\frac{T}{T_{ref}}\right) + s_{i,ref} - R \ln x_i \quad (15)$$

where  $T_{ref}$ ,  $h_{i,ref}$  and  $s_{i,ref}$  are reference values. The heat capacity and gas constant are denoted by  $c_{pi}$  and  $R$ , respectively. The molar fraction of species  $i$  given by  $x_i$  is expressed as follows :

$$x_i = \frac{N_i}{N}, \quad \forall i \in \mathcal{I} \quad (16)$$

with  $N = \sum_{i \in \mathcal{I}} N_i$  the total molar number. Consequently, the enthalpy and the entropy can be expressed as follows :

$$H = \sum_{i \in \mathcal{I}} N_i h_i \quad (17)$$

$$S = \sum_{i \in \mathcal{I}} N_i s_i \quad (18)$$

It is worth noting that the entropy  $S$  (10) can be recovered from (18) by using (17) together with the chemical potential (De Groot & Mazur (1962); Sandler (1999))

$$\mu_i = h_i - T s_i, \quad \forall i \in \mathcal{I} \quad (19)$$

### 2.3 The irreversible entropy production $\Sigma_s$

Let us first rewrite the expression of the entropy production  $\Sigma_s$  given in (13) by :

$$\begin{aligned} \Sigma_s = & \sum_{i \in \mathcal{I}} \frac{F_{iI}}{T} \left( (h_{iI} - h_i) - T(s_{iI} - s_i) \right) \\ & + \left( \frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \right) + \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} rV \geq 0 \end{aligned} \quad (20)$$

where the chemical potential (19) has been used. We have the following property which represents the source of contributions to  $\Sigma_s$  (20).

*Property 1.* The irreversible entropy production  $\Sigma_s$  (20) is expressed as the sum of four thermodynamically separate contributions as follows :

$$\Sigma_s = \Sigma_s^{\text{mix.}} + \Sigma_s^{\text{heat conv.}} + \Sigma_s^{\text{heat ex.}} + \Sigma_s^{\text{reac.}} \geq 0 \quad (21)$$

where :

$$\Sigma_s^{\text{mix.}} = R \sum_{i \in \mathcal{I}} F_{iI} \left( \ln\left(\frac{N_{iI}}{N_I}\right) - \ln\left(\frac{N_i}{N}\right) \right) \quad (22)$$

$$\Sigma_s^{\text{heat conv.}} = \sum_{i \in \mathcal{I}} c_{pi} F_{iI} \left( \frac{T_I}{T} - 1 - \ln\left(\frac{T_I}{T}\right) \right) \quad (23)$$

$$\Sigma_s^{\text{heat ex.}} = \left( \frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \right) \quad (24)$$

and

$$\Sigma_s^{\text{reac.}} = \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} rV \quad (25)$$

are the irreversible entropy productions due to mixing, heat convection, heat exchange and chemical reaction, respectively. Furthermore, these physical effects are intrinsically independent from each other, each constituent

entropy production is therefore non-negative thanks to the second law of thermodynamics.

From a mathematical point of view, it is straightforward to show the non-negative definiteness properties of  $\Sigma_s^{\text{mix.}}$  (22),  $\Sigma_s^{\text{heat conv.}}$  (23) and  $\Sigma_s^{\text{heat ex.}}$  (24) (see also (Hoang *et al.* (2011)) for more details). Contrary to the entropy productions due to mixing  $\Sigma_s^{\text{mix.}}$ , heat convection  $\Sigma_s^{\text{heat conv.}}$  and heat exchange  $\Sigma_s^{\text{heat ex.}}$ , the entropy production resulting from the reaction  $\Sigma_s^{\text{reac.}}$  (25) depends only on the system state variables (*i.e.* the intensive variables vector  $w$  (4)) and the reaction rate  $rV$ . It is probably worth noting that the sign constraint on  $\Sigma_s^{\text{reac.}}$  can be proved but restricted to the neighborhood of the (stationary) equilibrium states when considering a linear phenomenological law for the reaction rate (De Groot & Mazur (1962)). In general, this sign constraint is difficult to be proven mathematically and it remains an open problem for the trajectories which are governed by the reaction system dynamics (5)-(7) subject to a given initial condition. Up to now, no general proof is available for the nonlinear case. Consequently, the non-negative property of  $\Sigma_s^{\text{reac.}}$  (25) has been largely accepted as an *a priori* postulate of irreversible thermodynamics (Favache & Dochain (2009)).

### 3. TOWARDS A THERMODYNAMICALLY STRUCTURED FORM OF THE REACTION RATE

In chemical reaction engineering, it is shown (Grmelà (2012); Hoang & Dochain (2013a)) that any reaction taking place in the reactor is induced by the chemical affinity (called the thermodynamic driving force (De Groot & Mazur (1962))). This force acts on the reaction rate when the system is outside the chemical equilibrium, through the generation of the interaction of the reactants (Sandler (1999)). Let us now introduce the definition of the total chemical affinity of the reversible reaction (1) :

$$\mathcal{A} = \mathcal{A}_f - \mathcal{A}_r \quad (26)$$

where :

$$\mathcal{A}_f = -\nu_A \frac{\mu_A}{T} \quad \text{and} \quad \mathcal{A}_r = \nu_B \frac{\mu_B}{T} \quad (27)$$

are the chemical affinities of the forward and reverse reactions, respectively.

The expression of  $\Sigma_s^{\text{reac.}}$  (25) can thus be rewritten with (26)(27):

$$\Sigma_s^{\text{reac.}} = \mathcal{A} rV \quad (28)$$

which is non-negative as previously mentioned. Note that the sign constraint of  $\Sigma_s^{\text{reac.}}$  (28) holds for any reaction kinetic constant. From this it is straightforward to show that the affinity  $\mathcal{A}$  and reaction rate  $rV$  have the same sign for any evolution; if  $\mathcal{A} > 0$  (resp.  $\mathcal{A} < 0$ ) then  $rV > 0$  (resp.  $rV < 0$ ) and if  $\mathcal{A} = 0$  then  $rV = 0$  when the chemical equilibrium is reached. In other words, the reaction always evolves in the direction of decreasing affinity.

*Remark 4.* Note that the affinity  $\mathcal{A}$  (26)(27) is also an intensive variable since  $\frac{\mu_i}{T}$  is an intensive variable,  $\forall i \in \mathcal{I}$  (see Remark 1). Consequently, it is shown that  $\mathcal{A}$  is a function of the extensive variable vector  $Z$  given in (4), *i.e.*  $\mathcal{A} = \mathcal{A}(Z)$ .

Let us restate the following lemma. This result is independent from the reaction kinetics. A complete version of

this lemma dedicated to multi-component mixtures can be found in (Hoang & Dochain (2013a)).

*Lemma 1.* The chemical affinity (26)(27) of the reversible reaction (1) fulfills the following inequality :

$$\nu_A \frac{\partial \mathcal{A}}{\partial N_A} + \nu_B \frac{\partial \mathcal{A}}{\partial N_B} \leq 0 \quad (29)$$

The following proposition gives a sufficient condition on the chemical reaction rate  $rV$  in order to guarantee the sign constraint of  $\Sigma_s^{\text{reac}}$ . (28) along the dynamical trajectories regardless of (29).

*Proposition 1.* The irreversible entropy production  $\Sigma_s^{\text{reac}}$ . (28) is non-negative if a structured representation through the reaction force is considered for the reaction rate  $rV$  subject to **(H3)** as follows :

$$rV = k_f(T) \left( \exp\left(\frac{\mathcal{A}_f}{R}\right) - \exp\left(\frac{\mathcal{A}_r}{R}\right) \right) \quad (30)$$

where the kinetic constant of the reversible reaction (1) is commonly given by the Arrhenius law :

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) > 0 \quad (31)$$

where  $k_0$  and  $E_a$  are the kinetic constant and activation energy, respectively.

**Proof.** The proof immediately follows.  $\square$

As a consequence of Proposition 1, we have the following corollary.

*Corollary 1.* The explicit expression of the reaction rate  $rV$  (30) presents the (generalized) mass-action law and is given as follows :

$$rV = k_f(T) \left(\frac{N_A}{N}\right)^{-\nu_A} - k_r(T) \left(\frac{N_B}{N}\right)^{\nu_B} \quad (32)$$

where the forward and reverse kinetic constants are :

$$\begin{cases} k_f(T) = k_{0f}(T) \exp\left(-\frac{E_{af}}{RT}\right) \\ k_r(T) = k_{0r}(T) \exp\left(-\frac{E_{ar}}{RT}\right) \end{cases} \quad (33)$$

with

$$\begin{cases} k_{0f}(T) = k_0 \left( \left(\frac{T}{T_{ref}}\right)^{\frac{\nu_A c_{pA}}{R}} \exp\left(\frac{-\nu_A(c_{pA} - s_{A,ref})}{R}\right) \right) \\ E_{af} = \nu_A(-c_{pA}T_{ref} + h_{A,ref}) + E_a \\ k_{0r}(T) = k_0 \left( \left(\frac{T}{T_{ref}}\right)^{\frac{-\nu_B c_{pB}}{R}} \exp\left(\frac{\nu_B(c_{pB} - s_{B,ref})}{R}\right) \right) \\ E_{ar} = -\nu_B(-c_{pB}T_{ref} + h_{B,ref}) + E_a \end{cases} \quad (34)$$

**Proof.** Let us first rewrite  $rV$  (30) by using (27) :

$$rV = k_0 \exp\left(-\frac{E_a}{RT}\right) \left( \exp\left(\frac{-\nu_A \mu_A}{R T}\right) - \exp\left(\frac{\nu_B \mu_B}{R T}\right) \right) \quad (35)$$

From (19) we have  $\frac{\mu_i}{T} = \frac{h_i}{T} - s_i$ ,  $\forall i \in \mathcal{I}$ . By considering (14)(15) we have :

$$\begin{aligned} \frac{\mu_i}{T} &= -c_{pi} \ln\left(\frac{T}{T_{ref}}\right) + (c_{pi} - s_{i,ref}) \\ &\quad + \frac{-c_{pi}T_{ref} + h_{i,ref}}{T} + R \ln\left(\frac{N_i}{N}\right), \forall i \in \mathcal{I} \end{aligned} \quad (36)$$

(35)(36) end the proof.  $\square$

*Remark 5.* In the neighborhood of the (stationary) equilibrium, it is shown by considering the first-order Taylor expansion (of the exponential functions  $\exp\left(\frac{\mathcal{A}_f}{R}\right)$  and  $\exp\left(\frac{\mathcal{A}_r}{R}\right)$ ) together with (26) that there exists a positive constant  $K_r$  such that (30) reduces to :

$$rV = K_r \mathcal{A} \quad (37)$$

with  $K_r = \frac{k(T)}{R} > 0$ . On the one hand, (37) typically form an usual connection between the flow variable (reaction rate) and corresponding effort variable (reaction force) required for Bond-graph modeling of the underlying physical phenomena (Couenne *et al.* (2006)). On the other hand, (37) represents the linear phenomenological law of irreversible thermodynamics for the chemical transformation (De Groot & Mazur (1962)).

#### 4. AN AFFINITY-BASED CANDIDATE LYAPUNOV FUNCTION

Similarly to gravity, (linear) spring and electric forces which give rise to a potential, the reaction force  $\mathcal{A}$  involved in chemical reaction systems can also be viewed as the gradient of a potential function  $\mathcal{P}(\mathcal{A})$  with respect to the deviation of the reaction system from its chemical equilibrium (*i.e.* the affinity  $\mathcal{A}$ ) as follows (Grmela (2012)) :

$$\mathcal{A} \equiv -\frac{d\mathcal{P}(\mathcal{A})}{d\mathcal{A}} \quad (38)$$

Consequently, we derive :

$$\mathcal{P}(\mathcal{A}) = -\frac{1}{2} \mathcal{A}^2 \quad (39)$$

*Remark 6.* The sign  $\prec - \succ$  in (38) shows that if the chemical equilibrium of an isolated system is disturbed by changing the internal conditions, the reaction force acts in the direction to counteract the change (*i.e.* pushing the reaction system back to its chemical equilibrium) in accordance to the Le Chatelier's Principle.

*Remark 7.* The potential function  $\mathcal{P}(\mathcal{A})$  (39) meets the so-called thermodynamically stable evolution criterion (Hoang & Dochain (2013a)) :

$$\left(-\nu_A \frac{\partial \mathcal{P}(\mathcal{A})}{\partial N_A} - \nu_B \frac{\partial \mathcal{P}(\mathcal{A})}{\partial N_B}\right) rV \leq 0 \quad (40)$$

Since the reaction system is open through the material and heat exchanges at its surrounding surface, the stationary equilibrium (in the sense of system theory) may not coincide with the chemical equilibrium (*i.e.*  $r = 0$ ). As a consequence and for the sake of coherence with thermodynamics through the potential function  $\mathcal{P}(\mathcal{A})$  (39), a particularly useful candidate for the stability analysis and control design of the reaction system dynamics (5)-(7) is the following function :

$$W(\mathcal{A}(Z), \mathcal{A}(Z_d)) = \frac{1}{2} \left( \mathcal{A}(Z) - \mathcal{A}(Z_d) \right)^2 \geq 0 \quad (41)$$

where  $Z_d$  is the reference stationary equilibrium (*i.e.*  $\frac{dZ_d}{dt} \equiv 0$ ).

The geometrical property of the non-negative function  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  is shown in the following proposition.

*Proposition 2.*  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  (41) measures the algebraic distance between the concave potential function  $\mathcal{P}(\mathcal{A})$  (39) and its tangent hyperplane passing through

$\mathcal{A}_d = \mathcal{A}(Z_d)$ . Furthermore,  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  is a convex function.

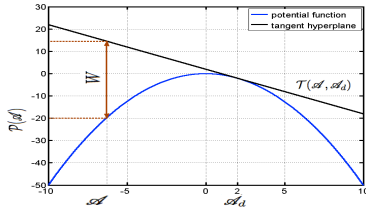


Fig. 1. The potential function and its tangent hyperplane

**Proof.** First note that the tangent hyperplane passing through  $\mathcal{A}_d$  of the potential function  $\mathcal{P}(\mathcal{A})$  (39) is

$$\mathcal{T}(\mathcal{A}, \mathcal{A}_d) = \left. \frac{d\mathcal{P}(\mathcal{A})}{d\mathcal{A}} \right|_{\mathcal{A}=\mathcal{A}_d} (\mathcal{A} - \mathcal{A}_d) + \mathcal{P}(\mathcal{A}_d)$$

From the concavity of the the potential function  $\mathcal{P}(\mathcal{A})$  (39), the algebraic distance is given by (see Figure 1) :

$$W(\mathcal{A}(Z), \mathcal{A}(Z_d)) = \mathcal{T}(\mathcal{A}, \mathcal{A}_d) - \mathcal{P}(\mathcal{A}) \geq 0$$

which leads to (41). This concludes the proof.  $\square$

Thanks to the non-negative definiteness property (41), the convex function  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  can then be used for the control design of the unstable CSTR via the controlled reaction rate.

*Theorem 1.* Let  $\Pi = \{Z \mid W(\mathcal{A}(Z), \mathcal{A}(Z_d)) = 0\}$  be the (largest) invariant set of the dynamics (5)-(7). We have :

$$\Pi = \left\{ Z \mid Z = \gamma Z_d, \forall \gamma \in \mathcal{R}^{*+} \right\} \quad (42)$$

where the positive scalar  $\gamma$  is called the homogeneity ratio. Consequently, the system dynamics (5)-(7) with the reaction rate  $rV$  (30)(31) is globally asymptotically stabilized at the desired reference state  $Z_d$  if

$$\begin{cases} \frac{dW}{dt} < 0, \forall t \geq 0, Z \notin \Pi \\ \frac{dW}{dt} \rightarrow 0 \text{ as } t \rightarrow +\infty \text{ and } Z \in \Pi \end{cases} \quad (43)$$

and

$$\gamma = 1 \quad (44)$$

**Proof.** Due to the homogeneous property of degree 0 of the chemical affinity  $\mathcal{A}(Z)$  with respect to  $Z$  (see Remark 4), it is shown that :

$$\mathcal{A}(\gamma Z) = \mathcal{A}(Z), \forall \gamma \in \mathcal{R}^{*+}$$

which provides the largest invariant set  $\Pi$  as given in (42). Consequently, the set  $\Pi$  is reduced to the only point  $Z_d$  when the ratio of homogeneity  $\gamma$  fulfils the condition (44). Together with (43),  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  (41) qualifies as a Lyapunov function. Asymptotic stability follows immediately by invoking La Salle's invariance principle (Khalil (2002)) and (44).  $\square$

*Remark 8.* From (44), we obtain :

$$\frac{Z}{Z_d} = 1 \Leftrightarrow \frac{H}{H_d} = \frac{N_A}{N_{Ad}} = \frac{N_B}{N_{Bd}} = 1 \quad (45)$$

The above proportions consequently provide<sup>3</sup> :

<sup>3</sup> A trivial case is to impose  $H = H_d$  and/or  $N_A = N_{Ad}$  and/or  $N_B = N_{Bd}$  on the reaction system. Consequently, no feedback

$$\frac{m}{m_d} = \frac{N}{N_d} = 1 \quad (46)$$

From this it is shown that the strict convexity of the  $W(\mathcal{A}(Z), \mathcal{A}(Z_d))$  (41) can be obtained if at least one extensive quantity (for instance, the total mass  $m$  or total mole number  $N$  etc.) is fixed. This analysis meets the result presented in (Ydstie & Alonso (1997); Jillson & Ydstie (2007); Hoang *et al.* (2012)).

Let us illustrate some thermodynamic concepts and the above developments on a simple example.

*Example 1.* For the sake of simplicity and illustration, let us consider a vector-valued function in  $\mathcal{R}^2$  as follows :

$$v(x_1, x_2) = \left( v_1(x_1, x_2), v_2(x_1, x_2) \right)^T \quad (47)$$

where :

$$\begin{cases} v_1(x_1, x_2) = -\ln\left(\frac{x_1}{x_1 + x_2}\right) \\ v_2(x_1, x_2) = -\ln\left(\frac{x_2}{x_1 + x_2}\right) \end{cases} \quad (48)$$

We can check easily that the vector-valued function  $v(x_1, x_2)$  (47)(48) is homogeneous of degree 0 and consequently,  $v_1(x_1, x_2)x_1 + v_2(x_1, x_2)x_2$  is a homogeneous function of degree 1 with respect to  $(x_1, x_2)$ .

The affinity-like function is defined as a weighted sum (or conical combination) of the homogeneous functions of degree 0,  $v_1(x_1, x_2)$  and  $v_2(x_1, x_2)$  (see (26)(27)) as follows :

$$\mathcal{A}(x_1, x_2) = \delta_1 v_1(x_1, x_2) + \delta_2 v_2(x_1, x_2), \delta_1, \delta_2 \in \mathcal{R} \quad (49)$$

From this the (non-negative) storage function  $W(x_1, x_2) = \frac{1}{2} \left( \mathcal{A}(x_1, x_2) - \mathcal{A}(x_{1d}, x_{2d}) \right)^2$  (41) is explicitly given by :

$$W(x_1, x_2) = \frac{1}{2} \left( \delta_1 \ln\left(\frac{x_1}{x_1 + x_2} \frac{x_{1d} + x_{2d}}{x_{1d}}\right) + \delta_2 \ln\left(\frac{x_2}{x_1 + x_2} \frac{x_{1d} + x_{2d}}{x_{2d}}\right) \right)^2 \quad (50)$$

where (48) has been used.

Figure 2 shows the geometrical shape of  $W(x_1, x_2)$  (50) with a desired reference state assumed to be  $(x_{1d}, x_{2d}) = (15, 25)$ . As previously shown, the homogeneity ratio is determined by the following relation :

$$\frac{x_1}{x_{1d}} = \frac{x_2}{x_{2d}} \Leftrightarrow x_2 = \frac{x_{2d}}{x_{1d}} x_1 \quad (51)$$

Let  $x = (x_1, x_2)$  and assume that the dynamics of the storage function  $W(x)$  is such that (43) holds, the two following different scenarios can then be involved :

- If  $x$  is initialized at  $x^0$  (for example,  $x^0 = (20, 3)$  as shown with a red-colored point in Figure 2) and no constraint is imposed then the dynamics of  $x$  may converge to any point lying on the homogeneity ratio (including the desired point  $x_d$ ).
- If the constraint  $x_1 + x_2 = \text{const}$  is imposed and  $x$  is initialized at  $x^0 = (30, 10)$  as shown with a blue-colored point in Figure 2, then the dynamics of  $x$  asymptotically converges to the only point  $x_d$  since the homogeneity ratio  $\gamma$  equals 1.

control law is necessary since the system reaches its stationary equilibrium.

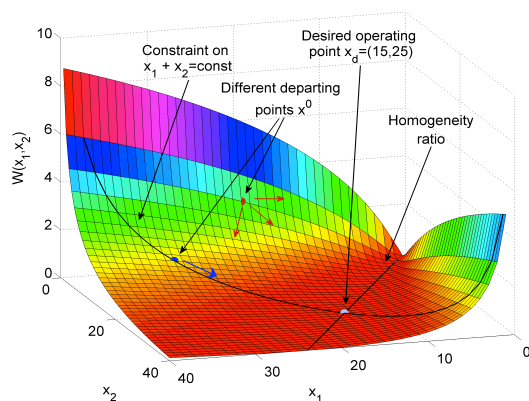


Fig. 2. An illustrative example with  $-\delta_1 = \delta_2 = 1$

## 5. CONCLUSION

In this work, we have shown how to control the reaction rate (central to generate the dynamical behavior of reaction systems, and in particular of the CSTR) at any desired stationary equilibrium by means of the Lyapunov-based method together with irreversible thermodynamics. More precisely, a structured representation of the reaction rate which presents the (generalized) mass-action law is proposed on the basis of the reaction force in order to guarantee the sign constraint of the irreversible entropy production due to the reaction. In this framework, the control of the reaction rate consists in controlling the reaction force through the use of an affinity-related candidate Lyapunov function. Future work will aim at the application of the proposed results to the stabilization of the unstable CSTR with possibly multiple chemical reactions. Besides, a comparison in terms of (uncontrolled/controlled) process dynamics characteristics with another structured form of the reaction rate (e.g. (Grmela (2012))) has to be studied.

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