Physica A 389 (2010) 3476–3483

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Thermodynamic performance *vs.* dynamic stability in an enzymatic reaction model

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ARTICLE INFO

Article history:
Received 28 January 2010
Received in revised form 18 March 2010
Available online 22 April 2010

Keywords:
Optimality
Nonlinear dynamics
Biochemistry
Enzyme kinetics

ABSTRACT

Previous studies on thermal engine models and energy-converting biological systems have shown that some of the parameters affecting their thermodynamic performance also affect their dynamic stability. In some cases, such parameters represent a tradeoff between these two generic properties. In the present work we carry out a similar analysis on a simple model for an enzymatic reaction. Despite its simplicity, this model captures the essential characteristics of numerous biochemical reactions where an endothermic reaction is made possible by coupling it (via an enzyme) with an exothermic reaction. Our results indicate that the global reaction chemical potential gap (Δ) affects both the thermodynamic properties and stability of the steady state. Larger Δ values imply a higher power output and a higher efficiency, but also a less strongly stable steady state.

1. Introduction

An optimally performing energy-converting system should fulfill at least two different sorts of good design principles: the system has to be dynamically robust, and it has to have optimal thermodynamic properties. Dynamic robustness is important because it allows the system to maintain its function despite internal and external perturbations. The robustness of a system usually manifests itself by the existence of a strongly stable dynamic attractor, that can be either a stable steady state or a stable (oscillatory) limit cycle. On the other hand, having a dynamically robust energy-converting system is not enough. The steady-state operation regime needs to have optimal thermodynamic properties as well: high power output, high efficiency, low entropy production, etc.

Recent studies on finite-time thermodynamic engines and heat pumps have shown that their stability and their thermodynamic performance are often governed by the same parameters. Indeed, the system stability usually weakens as its thermodynamic properties improve [1–13]. In consequence, such parameters need to be tuned to achieve an optimal tradeoff between favorable thermodynamic and dynamic properties. Similar studies on the stretch-reflex regulatory pathway and on a simple Brownian motor have confirmed these findings [14,15], in agreement with the notion that good design principles are usually shared by both artificial and biological systems [16].

We analyze in this work the stationary thermodynamic properties and the stability of a simple model for an enzymatic reaction. Despite its simplicity, such a model captures the essential characteristics of numerous biochemical reactions in which an endothermic reaction is made possible by coupling it (via an enzyme) with an exothermic reaction. These considerations make us believe that the present work results are relevant in a biological context.

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doi:10.1016/j.physa.2010.04.006

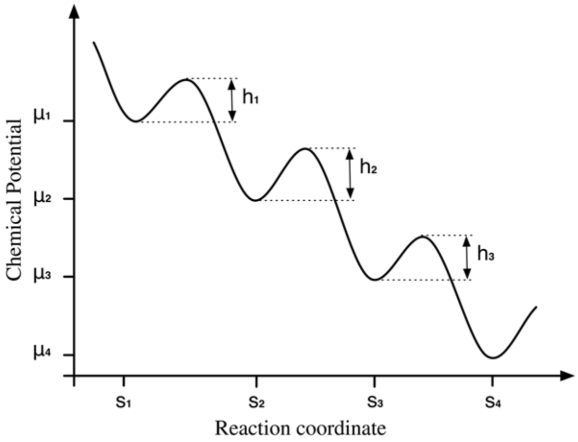

Fig. 1. Chemical potential profile necessary for the reactions in (1) to proceed forwards.

This paper is organized as follows: In Section 2 we introduce the enzymatic reaction model. In Section 3 we find the model steady state and analyze its stability locally. Finally, we discuss the obtained results in Section 4.

2. Model development

Definitions

Consider the following reaction scheme which corresponds to an endothermic reaction coupled with *ATP* hydrolysis (which is exothermic) via an enzyme [17].

$$E + X + ATP \rightleftharpoons E^P : X + ADP \rightleftharpoons E : Y + P_i + ADP \rightleftharpoons E + Y + P_i + ADP. \quad (1)$$

Due to the free energy balance, the resulting global reaction is exothermic. The chemical species in (1) are as follows: E denotes the enzyme, X is the substrate of the endothermic reaction, Y corresponds to the endothermic reaction product, $E^P : X$ indicates the complex formed by the phosphorylated enzyme and substrate X, $E : Y$ represents the complex formed by the enzyme and the product Y, *ATP* is adenosine triphosphate, *ADP* means adenosine diphosphate, and P_i corresponds to inorganic phosphate.

Reaction kinetics

Let S_i $(i = 1, \dots, 4)$ denote the ith state along the reaction sequence (1), and let μ_i be the corresponding chemical potential. In order for the reaction to proceed forwards it is necessary that $\mu_1 > \mu_2 > \mu_3 > \mu_4$. That is, the chemical potential profile must be like that pictured in Fig. 1. Bear in mind that intermediate states coincide with local minima of chemical potential [18].

From Arrhenius equation, the net velocities for the three reaction in (1) are [18]:

$$\nu_i = \xi_i \left(\mathrm{e}^{-h_i/RT} - \mathrm{e}^{-(h_i+\mu_i-\mu_{i+1})/RT} \right),$$

where $i = 1, 2, 3$, R is the gas constant, and T is the temperature. After factorizing $\exp(-h_i/RT)$ the above equation can be rewritten as

$$\nu_i = A_i \left(1 - \mathrm{e}^{-(\mu_i-\mu_{i+1})/RT} \right),$$

with $A_i = \xi_i \exp(-h_i/RT)$.

For the sake of simplicity assume that $A_1 = A_3 = A$ and define $\alpha = A_2/A$. These assumptions allow us to rewrite the chemical reaction velocities as

$$\nu_1 = A \left(1 - \mathrm{e}^{-(\mu_1-\mu_2)/RT} \right), \quad (2)$$

$$\nu_2 = \alpha A \left(1 - \mathrm{e}^{-(\mu_2-\mu_3)/RT} \right), \quad (3)$$

$$\nu_3 = A \left(1 - \mathrm{e}^{-(\mu_3-\mu_4)/RT} \right). \quad (4)$$

Assume now that the substrate and end-product concentrations are kept fixed, and that *ATP* is constantly synthesized from *ADP* and P_i, so that μ_1 and μ_4 remain constant. Conversely, μ_2 and μ_3 freely evolve until the system reaches the steady