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Effect of mesoscopic conservative phenomena in the dynamics of chemical reactions at the macroscopic scale☆

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HIGHLIGHTS

- Mesoscopic conservative phenomena can be implicit in macroscopic reaction rates.
- An isolated reacting system may have increments in the entropy production.
- A formulation of the dynamics that enhances the stability analysis is proposed.
- Coupling in reaction networks as a source of instability is pointed out.

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ABSTRACT

This paper studies the influence of conservative phenomena at the mesoscopic scale that affect the behavior of macroscopic variables in chemical reactions, generally understood as purely dissipative processes and whose mathematical formulation is usually derived using macroscopic variables. It is shown that conservative phenomena at the mesoscopic scale can affect the entropy production by transiently "pulling away" the system from the thermodynamic equilibrium. Two case studies are presented to illustrate this fact: the first one is an isolated system with a single reaction including two different scenarios, a purely dissipative reaction; and a second one that considers the influence of conservative elements at the mesoscopic scale. The second case generalizes the results to multiple reactions.

1. Introduction

The non-linear nature of chemical reactions along with their activated behavior have been common difficulties to model dynamics with enough physical consistency for several applications where stability properties are of special concern. For instance, in process control several approaches where the dissipative properties of chemical reactions have been exploited using thermodynamic properties as state variables [2–5], but only recently the importance of using thermodynamically consistent reaction rates has been recognized, motivating the use of potential driven expressions to formulate mass action kinetics [6–8]. A thermodynamically consistent formulation of the kinetics can generate new insights in the study of stability properties of chemical reaction networks if transient properties such as energy dissipation or entropy production are

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computed [9,10]. Also, many hypothetical reaction models that qualitatively reproduce experimentally observed complex dynamics such as chaos or oscillations have been proposed (*e.g.*, the Brusselator in [11]), and although these models have been helpful to understand the importance of the reaction mechanisms in the stability properties, their physical interpretation still might not be complete.

For a more thoughtful stability analysis, then detail of the transition from reactants into products should be considered at some degree. A direct macroscopic formulation, specially using empiric expressions, may lack information of the energetic transitions that could lead to less accurate entropy production rates. A summary of the mesoscopic phenomena should be considered for the macroscopic formulation [12].

There are several approaches to obtain a mesoscopic description of physical phenomena depending on the desired level of detail, *i.e.*, some are "more microscopic" than others. The use of extended state spaces in order to introduce fluctuations or detail of the fluxes [13], specifically the reaction rates as independent state variables has been studied, allowing a description for both fast and slow variables, and fluctuations due to random forces [14] or coupling it with mechanics, for instance [15]. Other approaches that result in a stochastic description of the dynamics have been made [12,16,14,17].

On the other hand, with the use of internal variables, de Groot and Mazur (see [18]) showed that the nonlinear relation between the driving forces and the kinetics expressions for chemical reactions at macroscopic scale can be derived by considering a linear relation of the driving forces at the mesoscopic scale. This approach was further developed in [19,20,17] to derive thermodynamically consistent expressions, in a formalism known as mesoscopic non-equilibrium thermodynamics (MNET), an extension to classical linear non-equilibrium thermodynamics that considers nonlinear force–flux relations. Some of the applications using internal variables can range from the description of intermediate states in a chemical reaction, dipole orientation in an electric field, conformational stages in a macromolecule, among others.

The conservative phenomena affect the stability properties specially far from the thermodynamic equilibrium and in this regard, in [21] a methodology to analyze the stability and passivity properties of thermodynamic systems has been proposed by considering the entropy production as a Lyapunov or a storage candidate function [1,22,23]. Following this idea, this contribution analyzes the effect of the conservative dynamics at the mesoscopic scale on the stability and convergence properties at the macroscopic scale using a particular reformulation of the reaction dynamics that enhances the stability analysis. Thus, the purpose of this paper is to show how conservative phenomena at the mesoscopic scale can influence the macroscopic variables, in particular it is shown that the entropy production for isolated reacting systems can transiently increase, due to the reversible energy conversions that occur when an energy barrier is present, producing also diverse qualitative behaviors in macroscopic variables such as conversion and temperature.

This paper is organized as follows. In Section 2, the class and the properties of the thermodynamic systems considered are defined and analyzed. In Section 3 following the MNET approach proposed by [19,20,17] we derive a reaction rate considering a reversible phenomenon when an energy barrier is present using an alternative definition for the mesoscopic affinity along the reaction path. Then, in Section 4, an entropic formulation for macroscopic phenomena is proposed, showing how the mesoscopic conservative phenomena can manifest in macroscopic systems far from equilibrium. Finally, in Section 5, two case studies are developed. First, two scenarios for a single reaction are considered: A purely dissipative reaction at the mesoscopic scale; and a case that considers the influence of a conservative element. Those scenarios are fully developed using the ideal gas state equation to easily compute all the thermodynamic properties. The second example generalizes the results to multiple reactions, leading to a quasi-quadratic structure whose stability properties can be analyzed through the elements of a computed matrix.

2. Spatially homogeneous reacting systems

Let us consider an isochoric isolated system Π assumed to be completely mixed. It is assumed that no spatial gradients are present, and the system Π can be fully characterized by two extensive properties: The moles, $\mathbf{N}$; and the total internal energy, $U = \mathbf{N}^{\mathrm{T}}\mathbf{u}$.[1] The internal energy vector is denoted by $\mathbf{u}$, thus the state vector is $\boldsymbol{\eta} = \operatorname{col}\{\mathbf{N},\ U\} \in \left(\mathbb{R}^n_{\geq 0} \times \mathbb{R}\right)$. The associated intensive properties vector is given by $\boldsymbol{\zeta} = \operatorname{col}\{-\boldsymbol{\mu}/T,\ 1/T\} \in (\mathbb{R}^n \times \mathbb{R}_+)$.

Since the system is isolated, the mass and internal energy of the system are constant, *i.e.*, given the initials mole vector, $\mathbf{N}_0$, and internal energy, U_0, it holds that $\mathbf{M}_w^{\mathrm{T}}\mathbf{N}_0 = \mathbf{M}_w^{\mathrm{T}}\mathbf{N}$ and $U_0 = U$, where $\mathbf{M}_w = \operatorname{col}\left\{m_{w,1},\ \ldots,\ m_{w,n}\right\}$ is the vector of molar masses. We consider that ω reversible chemical reactions involving n chemical species can take place in the system. Thus the dynamical behavior of the state vector is given by

$$\Pi\ :\ \dot{\boldsymbol{\eta}} = MV\mathbf{r}\left(\boldsymbol{\zeta}\right), \tag{1}$$

where $V \in \mathbb{R}_+$ is the volume, $\mathbf{r} : (\mathbb{R}^n \times \mathbb{R}_+) \to \mathbb{R}^\omega$ is the vector field of the specific chemical reactions kinetics, which are considered to be function of the intensive properties, and $M = \begin{pmatrix} \boldsymbol{\Gamma}^{\mathrm{T}} & \mathbf{0}^{\mathrm{T}}_{1\times\omega} \end{pmatrix}^{\mathrm{T}}$ is an interconnection matrix, where $\boldsymbol{\Gamma}$ is the stoichiometric matrix and $\mathbf{0}$ is a vector of zeros. The general chemical reaction used here is of the form

$$\mathbf{A}^{\mathrm{T}}\mathbf{E} \rightleftharpoons \mathbf{B}^{\mathrm{T}}\mathbf{E}, \tag{2}$$

[1] In order to simplify operations a vector notation is used, *e.g.*, $\mathbf{N}^{\mathrm{T}}\mathbf{u}$ instead of $\sum_{i=1}^{n} N_i u_i$. All vectors, including gradients, are column vectors.

where $\mathbf{E} = \text{col}\{E_1, \ldots, E_n\}$ is the vector of all chemical species. The stoichiometric coefficients for the k reactants and l products in the ith reaction are given by the sparse vectors $A_i = \text{col}\{\ldots, \alpha_{1,i}, \ldots, \alpha_{k,i}, \ldots\}$ and $B_i = \text{col}\{\ldots, \beta_{1,i}, \ldots, \beta_{l,i}, \ldots\}$, respectively. Thus, the elements of M when ω reactions are taking place inside the system are given by $\Gamma_i = B_i - A_i$,

$$M = \begin{pmatrix} \Gamma_1 & \Gamma_2 & \cdots & \Gamma_\omega \\ 0 & 0 & \cdots & 0 \end{pmatrix}. \tag{3}$$

Since no energy exchange is considered, the last row in M is null. Note that $\boldsymbol{\Gamma}\mathbf{r}(\boldsymbol{\zeta}) = \sum_{i=1}^{\omega} \Gamma_i r_i$ and due to the mass conservation principle, $\boldsymbol{\Gamma}^{\mathrm{T}}\mathbf{M}_w$ is equal to zero. In other words, for every reaction, we have $\Gamma_i^{\mathrm{T}}\mathbf{M}_w = 0$.

2.1. Entropy, conjugated forces and entropy production

According to the principles of thermodynamics, one can introduce, for any macroscopic system, a concave real-valued function $S : \mathbb{R}^{n+1} \to \mathbb{R}$ at least two times differentiable which depends on the extensive properties, which will be called entropy. The differential behavior of entropy can be computed through the Gibbs relation at constant volume ($dV = 0$) [24] as

$$dS = -\frac{\boldsymbol{\mu}^{\mathrm{T}}}{T} d\mathbf{N} + \frac{1}{T} dU. \tag{4}$$

Chemical reactions occur outside equilibrium, but once the local equilibrium hypothesis is assumed, it is possible to define macroscopic variables such as pressure and temperature in order to use Eq. (4) to compute finite time processes [18,25]. Depending on the particular configuration and characteristics of each system, the entropy gradient has the form

$$\boldsymbol{\zeta} \coloneqq \nabla S(\boldsymbol{\eta}) = \begin{pmatrix} -\dfrac{\boldsymbol{\mu}}{T} \\ \dfrac{1}{T} \end{pmatrix} \in \mathbb{R}^{n+1}. \tag{5}$$

It can be seen that Eq. (4) can also be written as $dS = \boldsymbol{\zeta}^{\mathrm{T}} d\boldsymbol{\eta}$, and, according to the properties of the entropy function, its Hessian is such that

$$\begin{aligned} \Omega &\coloneqq \nabla^2 S(\boldsymbol{\eta}) \\ &= \begin{pmatrix} \dfrac{\partial(-\boldsymbol{\mu}/T)}{\partial \mathbf{N}} & \dfrac{\partial(-\boldsymbol{\mu}/T)}{\partial U} \\ \dfrac{\partial(1/T)}{\partial \mathbf{N}} & \dfrac{\partial(1/T)}{\partial U} \end{pmatrix} < 0, \end{aligned} \tag{6}$$

due to the stability postulates [26]. The Onsager formulation for the entropy production (denoted here by $\Sigma \coloneqq \dot{S}$) states that, for closed systems, it is given by the product of the conjugated fluxes J_i and forces X_i (*e.g.*, a temperature gradient). Since the entropy is not a conservative variable, the total entropy balance for an isolated system is [20]:

$$\Sigma = \sum_i J_i X_i \geq 0, \tag{7}$$

where each flux is taken to be a linear combination of all forces, $J_i = \sum_i L_{ij} X_j$, and the Onsager (or reciprocal) relations are defined such that the entropy production is always positive and $L_{ij} = L_{ji}$ [27]. If there is only one phenomenon taking place, Eq. (7) becomes $\Sigma = LX^2 \geq 0$.

Using the entropy gradient, the entropy change in system Π is given by

$$\dot{S} = \boldsymbol{\zeta}^{\mathrm{T}} \dot{\boldsymbol{\eta}} = V \boldsymbol{\zeta}^{\mathrm{T}} M \mathbf{r}(\boldsymbol{\zeta}) \tag{8}$$

and since there is no interaction with the surroundings, there is no entropy flux present nor entropy production due to mixing processes. The total entropy production consists only of the internal entropy production due to the chemical reactions taking place in the system. Also note in Eq. (8) that

$$\boldsymbol{\zeta}^{\mathrm{T}} M = -\left(\boldsymbol{\Gamma}^{\mathrm{T}} \boldsymbol{\mu}\right)/T = -\boldsymbol{\mathcal{A}}/T, \tag{9}$$

where $\boldsymbol{\mathcal{A}} = \boldsymbol{\Gamma}^{\mathrm{T}} \boldsymbol{\mu}$ is the chemical affinity vector. Thus, the total entropy production is given by:

$$\Sigma = -V \boldsymbol{\mathcal{A}}^{\mathrm{T}} \mathbf{r}(\boldsymbol{\zeta})/T. \tag{10}$$

3. Mesoscopic scale reaction dynamics

By inspecting the expression of the macroscopic affinity, an homogeneous isolated chemical reaction at constant volume only dissipates energy. The transition from reactants to products should be described at a more detailed level, using the concept of *reaction path*, thus introducing an internal coordinate for a chemical reaction, which is independent of the

composition or the extent of the reaction. The adopted MNET approach presented by [18,17,20] introduces an internal coordinate γ, which is a *mesoscopic* measure of the progress of the reaction, with $\gamma = 0$ as the *state* of the pure reactants and $\gamma = 1$ as the *state* of the pure products. This approach can also include the influence of random fluxes, but for our purposes these shall not be considered in the following.

Under this framework, the mesoscopic affinity along the reaction path is:

$$\mathcal{A}_{rxn}(\gamma) - \mathcal{A}_{rxn}(0) = \Phi(\gamma) + RT \ln\left(\frac{c(\gamma)}{c(0)}\right), \tag{11}$$

where $\Phi(\gamma)$ is the energy barrier contribution to the chemical potential, or enthalpic contribution, assumed independent of the composition; $RT \ln(c(\gamma)/c(0))$ is the entropic contribution depending on the internal variable $c(\gamma)$, which defines the probability of finding the reaction complexes in a state $0 < \gamma < 1$ at a given moment. The probability $c(\gamma)$, associated to the concentration of the complexes, and the temperature T can be time dependent, while the internal coordinate γ is not part of the state variables $\boldsymbol{\eta}$ because of the local equilibrium assumption at this particular mesoscopic level.

It is assumed that there is a continuous sequence of states between the reactants with direct affinity $A^{\mathrm{T}}\boldsymbol{\mu} = \mathcal{A}_d = \mathcal{A}_{rxn}(0)$ and the products with reverse affinity $B^{\mathrm{T}}\boldsymbol{\mu} = \mathcal{A}_r = \mathcal{A}_{rxn}(1)$. The chemical affinity can be computed as $\mathcal{A} = \mathcal{A}_r - \mathcal{A}_d = \Gamma^{\mathrm{T}}\boldsymbol{\mu}$. On the other hand, the chemical potential vector is $\boldsymbol{\mu} = \boldsymbol{\mu}^{\mathrm{o}} + \ln(\mathbf{a})$, with $\boldsymbol{\mu}^{\mathrm{o}}$ as the vector of standard chemical potentials, which does not depend on the extent of the reaction, *i.e.*, is independent of composition, and $\ln(\mathbf{a}) = \mathrm{col}\{\ln(a_1), \ldots, \ln(a_n)\}$ is the vector of the natural logarithm of the activities.

Since both quantities should be equivalent, a link between the mesoscopic and macroscopic scale affinities, $\mathcal{A}_{rxn}(\gamma)$ and $\mathcal{A}$, was proposed in [7], such that

$$\mathcal{A}_{rxn}(\gamma) - \mathcal{A}_d = \varepsilon(\gamma)\,\mathcal{A}, \tag{12}$$

where the variable $\varepsilon(\gamma)$ is defined in such a way that $0 \leq \varepsilon(\gamma) \leq 1, \forall\gamma \in [0, 1]$, thus it is straightforward to define

$$\varepsilon(\gamma) := \frac{(\mathcal{A}_{rxn}(\gamma) - \mathcal{A}_{rxn}(0))}{(\mathcal{A}_{rxn}(1) - \mathcal{A}_{rxn}(0))}.$$

The hard-sphere collision theory of gas-phase reactions states that not all collisions produce a reaction, *i.e.*, they must collide with enough energy to exceed a threshold energy [28], which has been described using the well-known nonlinear Arrhenius expression. In a simple description of chemical reactions there is a conversion of kinetic energy (mainly translational and vibrational) to potential energy (mainly stored in the chemical bonds) as a reaction develops towards the activated complex, if an energy barrier is present [29]. Since the total energy is conserved, the potential energy is released again to kinetic energy continuously as composition changes, and its nature (translational, vibrational, rotational) depends on the particular geometry of the molecules [30]. Then, the conversion between kinetic energy and potential energy and vice-versa along the reaction path when overcoming the barrier can be seen as a reversible process at the mesoscopic scale. In order to include this reversible process under the MNET framework, we define

$$\Phi(\gamma) = \varepsilon(\gamma)\,\mathcal{A}^{\mathrm{o}} + RT \ln(\tau(\gamma)) + E_a(\gamma) \tag{13}$$

$$RT \ln\left(\frac{c(\gamma)}{c(0)}\right) = \varepsilon(\gamma)\left(\mathcal{A} - \mathcal{A}^{\mathrm{o}}\right) - RT \ln(\tau(\gamma)) - E_a(\gamma), \tag{14}$$

where $\mathcal{A}^{\mathrm{o}} = \mathcal{A}_r^{\mathrm{o}} - \mathcal{A}_d^{\mathrm{o}} = \Gamma^{\mathrm{T}}\boldsymbol{\mu}^{\mathrm{o}}$ is the standard chemical affinity, defined as the difference of the reverse and direct chemical affinities and is independent of the extent of the reaction, while both terms $RT \ln(\tau(\gamma))$ and $E_a(\gamma)$ are related to the energy barriers at a molecular level, whose value at the pure reactant and product states must be zero. Thus, when adding Equations (13) and (14), the reference $\varepsilon(\gamma)\,\mathcal{A}^{\mathrm{o}}$ and the energy barriers $E_a(\gamma)$ and $RT \ln(\tau(\gamma))$ cancel, remaining only $\varepsilon(\gamma)\,\mathcal{A}$, which is consistent with (12). In order to satisfy the energetic boundaries in the reaction path, $E_a(\gamma) = 0$ and $\tau(\gamma) = 1$ for $\gamma = 0, 1$, we choose the reference value $c(0) = \exp\left(\frac{\mathcal{A}_d - \mathcal{A}_d^{\mathrm{o}}}{RT}\right)$ in a similar way as in [20].

The cancellation of $RT \ln(\tau(\gamma))$ and $E_a(\gamma)$ when computing the mesoscopic scale chemical affinity is associated to the reversible phenomena at the mesoscopic scale. Also, adding and subtracting E_{a0} resembles the energy balance of some physical systems inspired in a Hamiltonian or Euler–Lagrange formulation where there is a conservative skew-symmetric interconnection matrix, which also results in adding and subtracting the reversible dynamics of the system [31].

On the other hand, it is postulated that the entropy production along the γ coordinate is the product of a flux, $r(\gamma)$, and a driving force, $-(\partial[\mu(\gamma)/T]/\partial\gamma)$ [20], *i.e.*,

$$\Sigma(\gamma) = -r(\gamma)\frac{\partial}{\partial\gamma}\left(\frac{\mathcal{A}(\gamma)}{T}\right), \tag{15}$$

which results from considering the flux–force relation

$$r(\gamma) = -l(\gamma)\frac{\partial}{\partial\gamma}\left(\frac{\mathcal{A}(\gamma)}{T}\right). \tag{16}$$

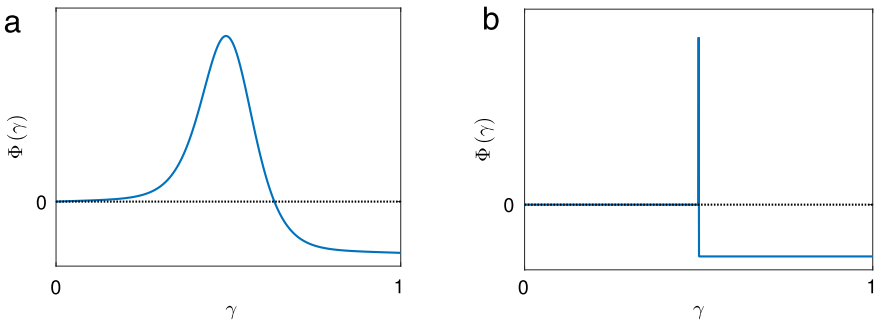

Fig. 1. The enthalpic energy barrier: (a) depicts the typical shape of a smooth stable transition, (b) shows the narrow peak when lumping the reaction rate to a macroscopic scale.

Note that Eq. (16) is in accordance with the Onsager's relations as in Eq. (7). Combining Eqs. (15) and (16), it can be seen that

$$\Sigma(\gamma) = l(\gamma)\left(\frac{\partial}{\partial\gamma}\left(\frac{\mathcal{A}(\gamma)}{T}\right)\right)^2 \geq 0,$$

where $l(\gamma)$ is assumed to be equal to $D_r c(\gamma)/R$, where D_r is a constant diffusion coefficient, $R = k_B N_{av}$ is the ideal gas constant, with k_B and N_{av} as the Boltzmann constant and the Avogadro number, respectively.

The entropy production at the mesoscopic scale must be equal to that at the macroscopic scale. If a quasi-stationary state at the mesoscopic scale is considered so that $r(\gamma) = r$, Eq. (15) can be integrated along the reaction path, which gives $\Sigma = -r(\mathcal{A}(1) - \mathcal{A}(0))/T = -r(\mathcal{A}/T)$, thus corresponding with Eq. (10).

3.1. Chemical reaction with a thermodynamic basis

In this subsection a thermodynamically consistent reaction rate is derived using the MNET approach [16,20], but now considering the energy barrier $E_a(\gamma)$ which was added and subtracted in the mesoscopic affinity. A steady state in the internal coordinate γ is considered since transitions in the reaction path occur in a faster time scale, thus lumping the reaction intermediates into reactants and products, which are the macroscopic observable species and the dependence of γ is dismissed in the resulting expression.

Then, solving for $c(\gamma)$ in Eq. (14) gives

$$c(\gamma) = \frac{c(0)}{\tau(\gamma)}\exp\left(\frac{\varepsilon(\gamma)(\mathcal{A} - \mathcal{A}^{\circ}) - E_a(\gamma)}{RT}\right) \tag{17}$$

and substituting into Eq. (16) yields the reaction rate in the mesoscopic scale

$$r(\gamma) = -D_r\frac{c(0)}{\tau(\gamma)}\exp\left(-\frac{\varepsilon(\gamma)\mathcal{A}^{\circ} + E_a(\gamma)}{RT}\right)\frac{\partial}{\partial\gamma}\exp\left(\frac{\mathcal{A}_{rxn}(\gamma) - \mathcal{A}_{rxn}(0)}{RT}\right). \tag{18}$$

Separating the energy barriers and the driving forces in the last equation and considering a quasi-stationary state along the reaction path, $r(\gamma) = r$, it is possible to integrate in the defined limits

$$r\int_0^1 \tau(\gamma)\exp\left(\frac{\varepsilon(\gamma)\mathcal{A}^{\circ} + E_a(\gamma)}{RT}\right)d\gamma = -D_r c(0)\exp\left(\frac{\mathcal{A}_{rxn}(\gamma) - \mathcal{A}_{rxn}(0)}{RT}\right)\Bigg|_0^1. \tag{19}$$

In order to evaluate the integrals, a delta function for the energy barrier is considered as shown in Fig. 1 since there is a narrow peak at the so-called transition state at $\gamma = \gamma_0$ [32,33], where the magnitude of the energy barriers are much larger than $\exp(\mathcal{A}^{\circ}/RT)$, then

$$\int_0^1 \tau(\gamma)\exp\left(\frac{\varepsilon(\gamma)\mathcal{A}^{\circ} + E_a(\gamma)}{RT}\right)d\gamma = \tau_0\exp\left(\frac{\varepsilon_0\mathcal{A}^{\circ} + E_{a0}}{RT}\right). \tag{20}$$

The intermediate species in $0 \leq \gamma \leq \gamma_0$ can be considered to be reactants, and intermediate species in $\gamma_0 \leq \gamma \leq 1$ can be considered products [17], this because the activated complex has the lowest probability, $c(\gamma_0)$, since in energetic terms the peak at γ_0 has been conceived as a saddle point. After some manipulations of Eqs. (19) and (20), the reaction rate is given by the following expression:

$$r(\boldsymbol{\zeta}) = \psi(\boldsymbol{\zeta})\left(r^+ - r^-\right), \tag{21}$$

where $r^+ = \exp\left(\frac{\mathcal{A}_d}{RT}\right)$ and $r^- = \exp\left(\frac{\mathcal{A}_r}{RT}\right)$, and the reaction *conductivity* is defined as

$$\psi(\boldsymbol{\zeta}) = \frac{D_r}{R\tau_0}\exp\left(-\frac{(\varepsilon_0\Gamma + A)^{\mathrm{T}}\boldsymbol{\mu}^{\circ} + E_{a0}}{RT}\right). \tag{22}$$

Expression (21) is consistent with the law of mass action, and only for $\mathcal{A} = 0$ it holds that $r(\boldsymbol{\zeta}) = 0$, or in other words, it satisfies the detailed balance principle. From now on, this macroscopic expression is independent of γ, and is important to highlight that although the force–flux relation along the reaction path is linear (Eq. (15)), it leads to an Arrhenius-like nonlinear expression when scaling to the macroscopic scale. In addition, even though the driving force at the macroscopic scale is the affinity $\mathcal{A}$, which depends on the chemical potential, in the kinetic expression (21) the canceled terms in the mesoscopic chemical affinity still appear, where τ_0 only affects the effective diffusion coefficient or pre-exponential factor defined as $D_r/R\tau_0$, while E_{a0} is present in the exponential function of the reaction conductivity. This can be associated to reversible or conservative processes at a molecular scale, only affecting the rate of the reaction but not the equilibrium itself.

For ω reactions, kinetic expression (21) can be generalized as[2]

$$\mathbf{r}(\boldsymbol{\zeta}) = \operatorname{diag}(\boldsymbol{\psi}(\boldsymbol{\zeta}))\left(\mathbf{r}^{+} - \mathbf{r}^{-}\right),$$

where $\boldsymbol{\psi}(\boldsymbol{\zeta}) = \operatorname{col}\{\psi_1(\boldsymbol{\zeta}), \ldots, \psi_\omega(\boldsymbol{\zeta})\}$ is the vector with the conductivity of each reaction, while $\mathbf{r}^{+}$ and $\mathbf{r}^{-}$ are the vectors of the forward and reverse rates, respectively. Finally, although the proposed mass action kinetics (21) is nonlinear with respect to chemical affinity, it can be rewritten as the product of the driving force and nonlinear terms:

$$r_i(\boldsymbol{\zeta}) = -\psi_i(\boldsymbol{\zeta})\,\vartheta_i(\boldsymbol{\zeta})\,\frac{\mathcal{A}_i}{RT}, \tag{23}$$

where

$$\vartheta_i(\boldsymbol{\zeta}) = \frac{r_i^{+} - r_i^{-}}{-\mathcal{A}_i/RT} = \exp\left(\frac{\mathcal{A}_{d,i} + \mathcal{A}_{r,i}}{2RT}\right)\frac{\sinh\left(-\frac{\mathcal{A}_i}{2RT}\right)}{-\mathcal{A}_i/2RT} \tag{24}$$

is positive definite since $\frac{\sinh(x)}{x} \geq 1$, therefore $\vartheta_i(\boldsymbol{\zeta}) \geq \exp\left(\frac{\mathcal{A}_{d,i}+\mathcal{A}_{r,i}}{2RT}\right) > 0$. For multiple reactions, a vector form for this expression is

$$\mathbf{r}(\boldsymbol{\zeta}) = -\operatorname{diag}(\boldsymbol{\psi}(\boldsymbol{\zeta}))\operatorname{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))\,\frac{\boldsymbol{\mathcal{A}}}{RT}, \tag{25}$$

with $\boldsymbol{\vartheta}(\boldsymbol{\zeta}) = \operatorname{col}\{\vartheta_1(\boldsymbol{\zeta}), \ldots, \vartheta_\omega(\boldsymbol{\zeta})\}$.

4. Entropy based representation of reacting systems

In this Section a special formulation of the reaction dynamics that leads to a quasi-quadratic expression for the entropy production, Σ, is presented, therefore being consistent with non-equilibrium processes, leading to a structure for the entropy production dynamics, $\dot{\Sigma}$, that facilitates the stability analysis. Then, relying on the basis of the fact that the vector field of specific macroscopic chemical reaction kinetics given in Eq. (25) is thermodynamically consistent, we propose that the spatially homogeneous isochoric isolated reacting system Π defined in Eq. (1) can be rewritten as

$$\dot{\boldsymbol{\eta}} = M\Psi(\boldsymbol{\zeta})M^{\mathrm{T}}\boldsymbol{\zeta}, \tag{26}$$

where $\Psi(\boldsymbol{\zeta})$ is a diagonal symmetric matrix, whose elements are equal to:

$$\Psi_{ii} = \frac{V}{R}\psi_i(\boldsymbol{\zeta})\,\vartheta_i(\boldsymbol{\zeta}) > 0; \quad \Psi_{ij} = 0,$$

being positive definite due to Eq. (24). This formulation enables us to rewrite the entropy production given in (10) in a quasi-quadratic form:

$$\Sigma = \boldsymbol{\zeta}^{\mathrm{T}}M\Psi(\boldsymbol{\zeta})M^{\mathrm{T}}\boldsymbol{\zeta} \geq 0, \tag{27}$$

where $M^{\mathrm{T}}\boldsymbol{\zeta} = \left[-\frac{\mathcal{A}_1}{T} \quad \ldots \quad -\frac{\mathcal{A}_\omega}{T}\right]^{\mathrm{T}}$ is the vector of the driving forces. Note that since matrix $\Psi(\boldsymbol{\zeta})$ is diagonal it has no skew-symmetric part, thus being consistent with the fact that macroscopically, chemical reactions are dissipative and therefore a globally decreasing function can be found [34].

It was shown in [7] that the entropy production for a chemical reaction with the form (21) is positive semi-definite. Using the same result for ω reactions and replacing the reaction rate vector (25) in Eq. (10) the entropy production is:

$$\begin{aligned}\Sigma &= 4VR\frac{\boldsymbol{\mathcal{A}}^{\mathrm{T}}}{2RT}\operatorname{diag}(\boldsymbol{\psi}(\boldsymbol{\zeta}))\operatorname{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))\,\frac{\boldsymbol{\mathcal{A}}}{2RT}\\ &= 4VR\sum_{i=1}^{\omega}\psi_i\exp\left(\frac{\left(\mathcal{A}_{d,i}+\mathcal{A}_{r,i}\right)}{2RT}\right)\frac{\mathcal{A}_i}{2RT}\sinh\left(\frac{\mathcal{A}_i}{2RT}\right) \geq 0,\end{aligned} \tag{28}$$

so the inequality in (27) holds for the kinetics derived in Section 3.

[2] Here diag $(\cdot)$ stands for a diagonal matrix of the argument vector.

In order to describe the dynamics of the entropy production, one must compute the gradient of Σ with respect to the state variables

$$\begin{aligned}\nabla\Sigma &= V\frac{\partial}{\partial\boldsymbol{\eta}}\left(\boldsymbol{\zeta}^{\mathrm{T}}M\mathbf{r}\left(\boldsymbol{\zeta}\right)\right)\\ &= V\left[\mathbf{r}^{\mathrm{T}}M^{\mathrm{T}}\left(\boldsymbol{\zeta}\right)+\left(\boldsymbol{\zeta}^{\mathrm{T}}M\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\left(\boldsymbol{\zeta}\right)\right)^{\mathrm{T}}\right]\Omega.\end{aligned} \tag{29}$$

Given that $\dot{\Sigma}=\left(\partial\Sigma/\partial\boldsymbol{\eta}\right)\dot{\boldsymbol{\eta}}$, or equivalently, $\dot{\Sigma}=\left(\nabla\Sigma\right)\left(VM\mathbf{r}\left(\boldsymbol{\zeta}\right)\right)$, the entropy production dynamics becomes

$$\dot{\Sigma}=V^{2}\left[\mathbf{r}^{\mathrm{T}}M^{\mathrm{T}}\Omega M\mathbf{r}+\left(\boldsymbol{\zeta}^{\mathrm{T}}M\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M\mathbf{r}\right]. \tag{30}$$

Because of the entropy Hessian properties, $\mathbf{r}^{\mathrm{T}}M^{\mathrm{T}}\Omega M\mathbf{r}$ is negative definite, while the sign of $\left(\boldsymbol{\zeta}^{\mathrm{T}}M\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M\mathbf{r}$ depends on the gradient $\nabla_{\boldsymbol{\zeta}}\mathbf{r}$, and therefore, on the nonlinearities of $\mathbf{r}\left(\boldsymbol{\zeta}\right)$.

According to the mean value theorem [35], and denoting with the subscript *eq* the equilibrium,

$$M\mathbf{r}\left(\boldsymbol{\zeta}\right)=A\left(\boldsymbol{\zeta}-\boldsymbol{\zeta}_{eq}\right)+\varkappa_{d}\left(\boldsymbol{\zeta}\right),$$

where

$$A=M\left[\frac{\partial\mathbf{r}\left(\boldsymbol{\zeta}\right)}{\partial\boldsymbol{\zeta}}\right]_{\boldsymbol{\zeta}_{eq}}$$

and

$$\varkappa_{d}\left(\boldsymbol{\zeta}\right)=\left(M\left[\frac{\partial\mathbf{r}\left(\boldsymbol{\zeta}\right)}{\partial\boldsymbol{\zeta}}\right]_{z(\boldsymbol{\zeta})}-A\right)\left(\boldsymbol{\zeta}-\boldsymbol{\zeta}_{eq}\right),$$

with $z\left(\boldsymbol{\zeta}\right)$ as a mean value between $\boldsymbol{\zeta}$ and $\boldsymbol{\zeta}_{eq}$. Hence, we have that

$$\lim_{\boldsymbol{\zeta}\to\boldsymbol{\zeta}_{eq}}\frac{\left\|\varkappa_{d}\left(\boldsymbol{\zeta}\right)\right\|}{\left\|\boldsymbol{\zeta}-\boldsymbol{\zeta}_{eq}\right\|}=0,$$

thus, near the equilibrium, it holds that

$$\lim_{\boldsymbol{\zeta}\to\boldsymbol{\zeta}_{eq}}\left\|M\left[\frac{\partial\mathbf{r}\left(\boldsymbol{\zeta}\right)}{\partial\boldsymbol{\zeta}}\right]_{z(\boldsymbol{\zeta})}\right\|=\left\|A\right\|,$$

and therefore

$$\left(\boldsymbol{\zeta}^{\mathrm{T}}M\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M\mathbf{r}\left(\boldsymbol{\zeta}\right)\leq-\left\|\Omega\right\|\left\|A\left(\boldsymbol{\zeta}-\boldsymbol{\zeta}_{eq}\right)\right\|^{2}\leq0.$$

Thus, we have that $\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)\left(M^{\mathrm{T}}\boldsymbol{\zeta}\right)\approx M\mathbf{r}\left(\boldsymbol{\zeta}\right)$, and the entropy production near the equilibrium can be approximated by

$$\dot{\Sigma}\approx2V^{2}\mathbf{r}^{\mathrm{T}}M^{\mathrm{T}}\Omega M\mathbf{r}\left(\boldsymbol{\zeta}\right)<0, \tag{31}$$

which can be used as a local Lyapunov function that guarantees the asymptotic stability of the equilibrium by standard Lyapunov stability arguments [23], as $\Sigma>0$ and $\dot{\Sigma}<0$ for $\mathbf{r}\neq0$.

However, when the system is far from equilibrium, the nonlinearities in $\mathbf{r}\left(\boldsymbol{\zeta}\right)$ may produce changes in the sign of (30). The equilibrium points of the reacting system (26) are given by the intersection of the submanifold defined by $\Gamma^{\mathrm{T}}\boldsymbol{\mu}_{eq}=\mathcal{A}_{eq}=0$, where $\boldsymbol{\mu}_{eq}$ and $\mathcal{A}_{eq}$ are the vector of chemical potentials and the affinity at the thermodynamic equilibrium, and the one given by mass balance $\Theta\left(\mathbf{N}-\mathbf{N}_{0}\right)=0$, where Θ is a constant matrix such that $\Theta^{\mathrm{T}}\Gamma=0$, restricting the admissible amounts of the chemical species.

5. Case studies

In this section two case studies are developed. First, a single reaction that results in a simple scalar stability analysis leading to the identification of conservative and dissipative mesoscopic phenomena is developed. The second example constitutes a general approach for several reactions rewriting the entropy production in a quasi-quadratic structure, whose stability properties are condensed in a computed matrix $Z\left(\boldsymbol{\zeta}\right)$ that shows which elements favor or impede convergence to the equilibrium.

5.1. Single reaction

For the sake of simplicity, and without loss of generality, it is assumed that all species are ideal gases obeying the state equation $pV = \mathbf{1}^{\mathrm{T}}\mathbf{N}RT$ where $\mathbf{1} \in \mathbb{R}^n$ is a vector of ones. With this consideration, the following thermodynamic properties can be easily computed

$$\begin{aligned} \boldsymbol{\mu}^{\mathrm{o}} &= \mathbf{u} - T\left(\mathbf{s}_{ref} - \mathbf{1}R + \int_{T_{ref}}^{T} \frac{\mathbf{c}_v}{T} dT\right), \\ \ln(\mathbf{a}) &= \ln\left(\mathbf{N}/N_{ref}\right), \\ \mathbf{u} &= \mathbf{u}_{ref} + \int_{T_{ref}}^{T} \mathbf{c}_v dT. \end{aligned} \tag{32}$$

Consider a single reaction

$$A^{\mathrm{T}}\mathbf{E} \rightleftharpoons B^{\mathrm{T}}\mathbf{E} \tag{33}$$

where $\mathbf{E}$ is the vector of all chemical species, while the stoichiometric coefficients for the k reactants and l products are given by the vectors $A = \mathrm{col}\{\alpha_1, \ldots, \alpha_k, 0_{n-k}\}$ and $B = \mathrm{col}\{0_k, \beta_1, \ldots, \beta_l, 0_{n-k-l}\}$, respectively. Note that, due to the stoichiometric invariant submanifold, given the initial condition $\boldsymbol{\eta}(0) = \mathrm{col}\{\mathbf{N}_0, U_0\}$, the process can be analyzed considering only one variable, for instance the extent of the reaction or conversion based on compound 1, *i.e.*, $\xi(t) = 1 - \frac{N_1(t)}{N_{1,0}}$, where $N_{1,0}$ is the initial moles of the first specie [36]. Then, the dynamical behavior reduces to a single equation

$$\dot{\xi}(t) = -\frac{V\alpha_1}{N_{1,0}} r(\boldsymbol{\zeta}), \tag{34}$$

where the remaining variables, $\mathbf{N}$, U, and $\boldsymbol{\zeta}$ can be seen as a function of the conversion.

Using the definition of $\vartheta(\boldsymbol{\zeta})$ given in Eq. (24), and since the reaction *conductivity* is greater than zero, the entropy production is computed as

$$\Sigma = -V\frac{\mathcal{A}}{T} r(\boldsymbol{\zeta}) = \frac{VRr^2(\boldsymbol{\zeta})}{\vartheta(\boldsymbol{\zeta})\psi(\boldsymbol{\zeta})} > 0 \quad \forall \mathcal{A} \neq 0,$$

and its dynamics is given by Eq. (30) with r as real-valued function, *i.e.*,

$$\dot{\Sigma} = \frac{V}{R}\vartheta(\boldsymbol{\zeta})\psi(\boldsymbol{\zeta})\left(M^{\mathrm{T}}\Omega M + W(\boldsymbol{\zeta})\right)\Sigma \tag{35}$$

where

$$W(\boldsymbol{\zeta}) = R\frac{\left(\nabla_{\boldsymbol{\zeta}} r(\boldsymbol{\zeta})\right)^{\mathrm{T}}}{\psi(\boldsymbol{\zeta})\vartheta(\boldsymbol{\zeta})}\Omega M. \tag{36}$$

Since $\frac{V}{R}\vartheta(\boldsymbol{\zeta})\psi(\boldsymbol{\zeta})\Sigma$ is positive definite for $\mathcal{A} \neq 0$, the sign of Eq. (35) depends only on the sign of $M^{\mathrm{T}}\Omega M + W(\boldsymbol{\zeta})$. In particular, since the Hessian is negative definite (see [7] for more details on the particular form of $\Omega < 0$ for the isochoric ideal gas case), the first term is negative definite, specifically

$$M^{\mathrm{T}}\Omega M = -\left(\frac{(\Delta_r u)^2}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2} + RA^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}A + RB^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}B\right),$$

where $\Delta_r u = \Gamma^{\mathrm{T}}\mathbf{u}$ is the change of internal energy in the reaction. These terms can be associated to the irreversible energetic changes and stoichiometric changes (which are pressure variations for this particular case) that aid the system to approach the thermodynamic equilibrium. To compute the second term, according to Eq. (36), it is necessary to compute the gradient of $r(\boldsymbol{\zeta})$

$$\nabla_{\boldsymbol{\zeta}} r(\boldsymbol{\zeta}) = \frac{\psi(\boldsymbol{\zeta})}{R}\begin{bmatrix} Br^- - Ar^+ \\ -\left((\varepsilon_0\Gamma + A)^{\mathrm{T}}\mathbf{u} + E_{a0}\right)\left(r^+ - r^-\right) \end{bmatrix},$$

therefore

$$\begin{aligned} W(\boldsymbol{\zeta}) = &-\frac{1}{\vartheta(\boldsymbol{\zeta})}\left[\frac{(\Delta_r u)^2}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2}\left(\varepsilon_0 r^+ + (1-\varepsilon_0)r^-\right) + R\left(A^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}Ar^+ + B^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}Br^-\right)\right] \\ &+ E_{a0}\frac{(\Delta_r u)}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2}\frac{\mathcal{A}}{RT}. \end{aligned} \tag{37}$$

The dynamics of the entropy production is similar to that in previous works [7,21] and consists of similar energetic and stoichiometric terms to those found in $M^{\mathrm{T}}\Omega M$, that can be associated to the irreversibility of the process, but now there is

Table 1
Parameters for the single reaction case.

Parameter	Value	Units
R	8.314	J/mol K
$\mathbf{s}_{ref}$ [a]	$(219\ 269\ 360\ 50)^{\mathrm{T}}$	J/mol K
$\mathbf{h}_{ref}$ [a]	$(52\ 83\ 29.8\ 15)^{\mathrm{T}} \times 10^3$	J/mol
$\mathbf{c}_v$ [a]	$(28\ 130\ 184\ 50)^{\mathrm{T}}$	J/mol K
ε_0	0.5	–
E_{a0}	222754	J/mol

[a] The reference values were taken from [37] (Ethylbenzene formation).

a new term where the energy barrier E_{a0} appears, whose sign cannot be determined *a priori*. To simplify the analysis it is convenient to define

$$\hat{W}(\boldsymbol{\zeta}) = E_{a0}\frac{(\Delta_r u)}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2}\frac{\mathcal{A}}{RT} \qquad \text{and} \qquad W^{-}(\boldsymbol{\zeta}) = W(\boldsymbol{\zeta}) - \hat{W}(\boldsymbol{\zeta}), \tag{38}$$

such that $W(\boldsymbol{\zeta})$ can be reformulated as the sum of the negative elements, W^{-}, plus the sign-undetermined term $\hat{W}(\boldsymbol{\zeta})$. In order to distinguish the contributions to the entropy production regardless the influence of the reaction *conductivity* $\psi(\boldsymbol{\zeta}) > 0$, whose value is affected by the presence of the energy barrier E_{a0}, one can define

$$\kappa(\boldsymbol{\zeta}) \coloneqq -\left(M^{\mathrm{T}}\Omega M + W^{-}(\boldsymbol{\zeta})\right)\frac{\vartheta(\boldsymbol{\zeta})}{R} > 0 \tag{39}$$

and

$$\chi(\boldsymbol{\zeta}) \coloneqq \hat{W}(\boldsymbol{\zeta})\frac{\vartheta(\boldsymbol{\zeta})}{R}. \tag{40}$$

The purpose of this is to rewrite the entropy production dynamics as the difference of the dissipative and the conservative terms, so that

$$\dot{\Sigma} = -V\psi(\boldsymbol{\zeta})\left[\kappa(\boldsymbol{\zeta}) - \chi(\boldsymbol{\zeta})\right]\Sigma. \tag{41}$$

Here $\chi(\boldsymbol{\zeta})$ has an undefined sign, and thus the difference $\kappa(\boldsymbol{\zeta}) - \chi(\boldsymbol{\zeta})$ has also an undetermined sign. If no energy barrier is present, the numerical value of E_{a0} is set to zero and the entropy production shall dissipate without sign changes in the time derivative of Σ since $\chi(\boldsymbol{\zeta})$ is not present. Then if $E_{a0} = 0$, the entropy production can be used as a Lyapunov function regardless on how far from equilibrium the system is (Fig. 2(a)). In general, all variables have a time evolution that resembles that of a first order process, for instance, the conversion in Fig. 3(a). Note also that $\kappa(\boldsymbol{\zeta})$ is always positive definite and reaches a limit positive value as time tends to infinity, while $\chi(\boldsymbol{\zeta}) = 0$ (Fig. 4(a)).

On the other hand, when the energy barrier is considered, the term $\chi(\boldsymbol{\zeta})$ is now present and its sign depends on the product $(\Delta_r u)\mathcal{A}$, then the difference in Eq. (41), $\kappa(\boldsymbol{\zeta}) - \chi(\boldsymbol{\zeta})$, might be negative far from equilibrium, thus reducing or even inverting the rate of convergence for the entropy production. In Fig. 2(b) the rate of the entropy production decreases for $t < t_a$, but later in $t_a < t < t_b$ there is an increment in the rate of the entropy production. This does not result in a violation of the second law since the entropy increases, the Gibbs energy decreases, and the Hessian is negative-definite by construction, but is rather the manifestation of the conservative phenomena at the mesoscopic scale. The values of $\Delta_r S$ or $\Delta_r G$ are unaltered by the presence of the energy barrier, since the equilibrium remains invariant under the presence of the reversible mesoscopic phenomena.

The conversion and temperature (not shown) have inflection points that coincide with the local maximum and minimum in the entropy production (Fig. 3(b)). The behavior of $\kappa(\boldsymbol{\zeta})$ in both scenarios is monotonically decreasing, since it does not include E_{a0} anywhere, but when $\chi(\boldsymbol{\zeta})$ is present, its magnitude and sign can exceed that of $\kappa(\boldsymbol{\zeta})$ (Fig. 4(a), (b)).

It is reasonable then to associate $\kappa(\boldsymbol{\zeta})$ with dissipative phenomena at mesoscopic and macroscopic scales, since it contains the linear contribution $\mathbf{r}^{\mathrm{T}}M^{\mathrm{T}}\Omega M\mathbf{r}$, associated to $M^{\mathrm{T}}\Omega M$, and the negative definite elements of the nonlinear contribution $\left(\boldsymbol{\zeta}^{\mathrm{T}}M\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M\mathbf{r}$, associated to $W^{-}(\boldsymbol{\zeta})$, while $\chi(\boldsymbol{\zeta})$ can be associated with the conservative phenomena at the mesoscopic scale, since it depends on E_{a0}.

When $t \gg t_b$ the system is close to the thermodynamic equilibrium and Eq. (31) becomes valid. The magnitude of the conservative term $\chi(\boldsymbol{\zeta})$ tends to zero near the equilibrium, meaning that the stored energy depletes and the behavior of Figs. 2(b), and 3(b) resemble that of Figs. 2(a) and 3(a). Thus somehow both processes, dissipation and conservation, are implicit in a single dynamic equation (see Eq. (34)) and, without dwelling too much into detail, the mesoscopic formalism from which the reaction rate is derived, is consistent enough to outline the transition state and therefore, to include the bulk effect of the reversible potential–kinetic mesoscopic energy conversions.

The numerical values used for this example are given in Table 1, thus displaying SI units in the case study Figures. The reference temperature and pressure are 298 K and 1 atm respectively and it was considered a 1 m^3 volume, with $D_r/R\tau_0$ equal to 7.605×10^6 1/s when $E_{a0} = 0$ and 1.521×10^{25} 1/s when $E_{a0} \neq 0$ in order to have similar time scales. The stoichiometric coefficients are $\Gamma^{\mathrm{T}} = (-1\ -1\ 1\ 0)$, which correspond to the reversible reaction $E_1 + E_2 \rightleftharpoons E_3$, with an inert specie E_4.

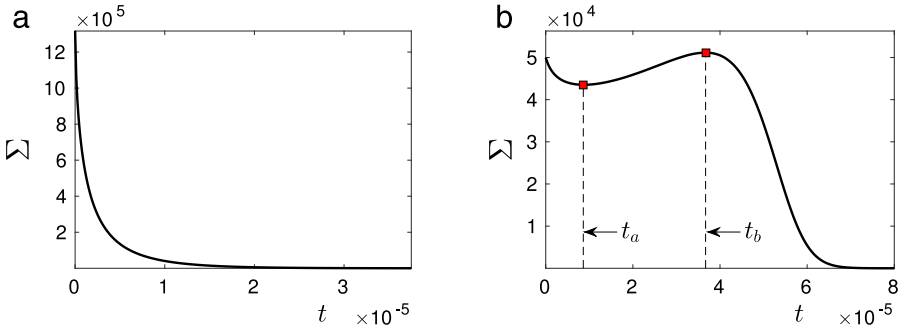

Fig. 2. Time evolution of Σ. In (a) the entropy production decays exponentially in the absence of E_{a0}, and (b) when E_{a0} is present, there is a time incremental of Σ in $t_a < t < t_b$ associated to the mesoscopic conservative phenomena.

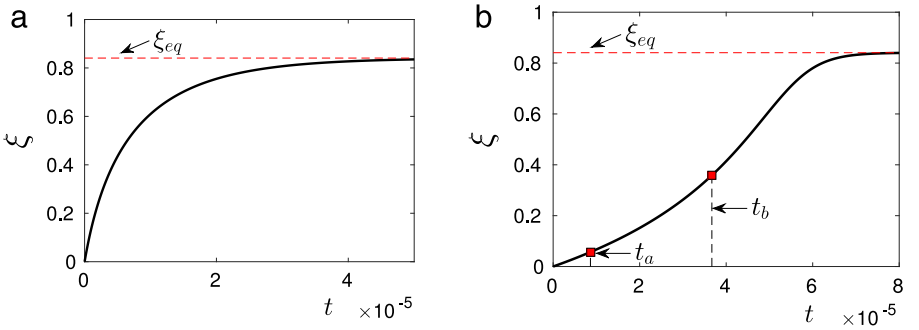

Fig. 3. Time evolution for ξ. In (a) the dynamics do not include E_{a0}, resembling first order kinetics, while in (b) the behavior resembles that of an overdamped second order kinetics. The temperature has a similar qualitative behavior (not shown).

5.2. Multiple reactions

When multiple reactions are taking place within the system, we can consider that the ith reaction has the same structure as in Eq. (21). The reaction conductivity $\psi_i(\boldsymbol{\zeta})$ can be expressed as $\psi_i(\boldsymbol{\zeta}) = \exp(\varphi_i(\boldsymbol{\zeta}))$, where $\varphi_i(\boldsymbol{\zeta})$ is a general energy barrier. Then the gradient for several reactions for the entropy production in Eq. (30) is

$$\nabla_{\boldsymbol{\zeta}}\mathbf{r} = \begin{pmatrix} \left(\frac{\mathbf{B}}{R}\mathrm{diag}\left(\mathbf{r}^{-}\right) - \frac{\mathbf{A}}{R}\mathrm{diag}\left(\mathbf{r}^{+}\right)\right)\mathrm{diag}\left[\boldsymbol{\psi}(\boldsymbol{\zeta})\right] \\ \frac{\partial\boldsymbol{\varphi}(\boldsymbol{\zeta})}{\partial\zeta_2}\mathrm{diag}\left(\mathbf{r}(\boldsymbol{\zeta})\right) \end{pmatrix}, \tag{42}$$

where $\boldsymbol{\varphi} = \mathrm{col}\{\varphi_1, \ldots, \varphi_\omega\}$ and it is assumed that $\boldsymbol{\varphi}$ is independent of the chemical potential, thus $\partial\varphi_i(\boldsymbol{\zeta})/\partial\boldsymbol{\zeta}_1 = \mathbf{0}$. Up to this point, no equation of state has been considered. In particular, for ideal gases the gradient of the energy barrier is

$$\frac{\partial\boldsymbol{\varphi}(\boldsymbol{\zeta})}{\partial\zeta_2} = \frac{1}{R}\left(\mathbf{u}^{\mathrm{T}}\left(\boldsymbol{\Gamma}\mathrm{diag}\left(\boldsymbol{\varepsilon}_0\right) + \mathbf{A}\right) + \mathbf{E}_{a0}^{\mathrm{T}}\right), \tag{43}$$

where $\mathbf{E}_{a0}$ is a vector of the energy barriers and $\boldsymbol{\varepsilon}_0 = \mathrm{col}\left\{\varepsilon_{0,1}, \ldots, \varepsilon_{0,\omega}\right\}$ is the vector of the fractions at which the activated complex is produced.

It is possible to rewrite the dynamics of the entropy production given in Eq. (30) as

$$\dot{\Sigma} = V^2\mathbf{r}^{\mathrm{T}}\mathbf{Z}(\boldsymbol{\zeta})\,\mathbf{r}, \tag{44}$$

where $\mathbf{Z}(\boldsymbol{\zeta}) = M^{\mathrm{T}}\Omega M + \mathbf{W}(\boldsymbol{\zeta})$. Using the definitions given in [21], it is possible to study its stability properties using the matrix $\mathbf{Z}(\boldsymbol{\zeta})$. Then the thermodynamic equilibrium of the reacting system is asymptotically stable if the symmetric part of $\mathbf{Z}(\boldsymbol{\zeta})$ is negative definite, *i.e.*,

$$\frac{\mathbf{Z}+\mathbf{Z}^{\mathrm{T}}}{2} = M^{\mathrm{T}}\Omega M + \frac{\mathbf{W}+\mathbf{W}^{\mathrm{T}}}{2} < 0, \tag{45}$$

or equivalently

$$-M^{\mathrm{T}}\Omega M > \frac{\mathbf{W}+\mathbf{W}^{\mathrm{T}}}{2}. \tag{46}$$

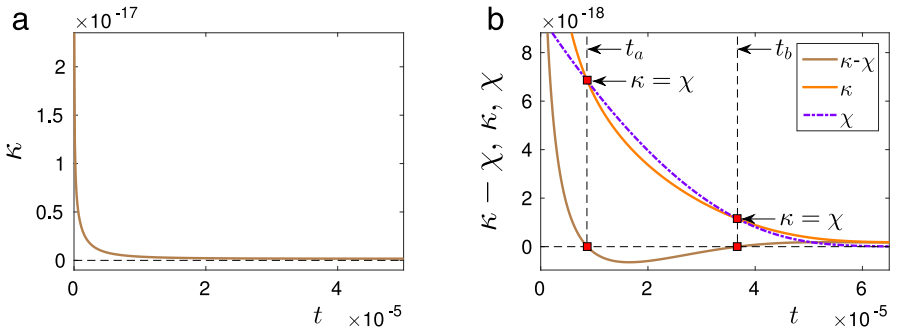

Fig. 4. The role of $\kappa(\boldsymbol{\zeta})$ and $\chi(\boldsymbol{\zeta})$: (a) dissipation of $\kappa(\boldsymbol{\zeta})$ when E_{a0} is not present, and (b) a "competition" between the dissipative and conservative dynamics when $\chi(\boldsymbol{\zeta})$ (and therefore E_{a0}) is present.

Here, because of the properties of the Hessian of the entropy, $M^{\mathrm{T}}\Omega M < \mathbf{0}$, $\mathbf{W}(\boldsymbol{\zeta})$ for multiple reactions has the following structure

$$\mathbf{W}(\boldsymbol{\zeta}) = [\mathrm{diag}(\mathbf{r})]^{-1}\mathrm{diag}\left(M^{\mathrm{T}}\boldsymbol{\zeta}\right)\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M. \tag{47}$$

Using Eq. (24) the above equation becomes

$$\mathbf{W}(\boldsymbol{\zeta}) = R[\mathrm{diag}(\boldsymbol{\psi}(\boldsymbol{\zeta}))\,\mathrm{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))]^{-1}\left(\nabla_{\boldsymbol{\zeta}}\mathbf{r}\right)^{\mathrm{T}}\Omega M,$$

where $\mathrm{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta})) := R\left[\mathrm{diag}\left(M^{\mathrm{T}}\boldsymbol{\zeta}\right)\right]^{-1}\mathrm{diag}\left(\mathbf{r}^{+}-\mathbf{r}^{-}\right) > I$ and I is the $\omega\times\omega$ identity matrix. Now, considering the gradient (42) and assuming ideal gas compounds, $\mathbf{W}(\boldsymbol{\zeta})$ has the following form

$$\begin{aligned}\mathbf{W}(\boldsymbol{\zeta}) = &-\frac{\Gamma^{\mathrm{T}}\mathbf{u}\mathbf{u}^{\mathrm{T}}\Gamma}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2}[\mathrm{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))]^{-1}\left[\mathrm{diag}(\boldsymbol{\varepsilon}_0)\,\mathrm{diag}\left(\mathbf{r}^{+}\right)+(I-\mathrm{diag}(\boldsymbol{\varepsilon}_0))\,\mathrm{diag}\left(\mathbf{r}^{-}\right)\right]\\ &-R\left(\mathbf{B}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{B}-\mathbf{A}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{B}\right)\mathrm{diag}\left(\mathbf{r}^{-}\right)[\mathrm{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))]^{-1}\\ &-R\left(\mathbf{A}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{A}-\mathbf{B}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{A}\right)\mathrm{diag}\left(\mathbf{r}^{+}\right)[\mathrm{diag}(\boldsymbol{\vartheta}(\boldsymbol{\zeta}))]^{-1}+\hat{\mathbf{W}}(\boldsymbol{\zeta}),\end{aligned} \tag{48}$$

where

$$\hat{\mathbf{W}}(\boldsymbol{\zeta}) = \left(\frac{\Gamma^{\mathrm{T}}\mathbf{u}}{\mathbf{N}^{\mathrm{T}}\mathbf{c}_v T^2}\right)\frac{\mathbf{E}_{a0}^{\mathrm{T}}\mathrm{diag}(\mathcal{A})}{RT}. \tag{49}$$

When a single reaction is considered, Eq. (48) reduces to Eq. (37). However, this is a more general case where the first term of Eq. (48) is similar to the first term of Eq. (37), while the second and third terms (more general than the second and third terms of Eq. (37)) do not have a well defined sign due to the cross terms such as $\mathbf{A}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{B}$ and $\mathbf{B}^{\mathrm{T}}[\mathrm{diag}(\mathbf{N})]^{-1}\mathbf{A}$. Finally, the last term, given in Eq. (49) is the generalization of Eq. (38) for multiple reactions and gives the contributions of the conservative phenomena at the mesoscopic scale through the energy barrier vector, $\mathbf{E}_{a0}$. As in the previous case this term has not a well defined sign.

The insights gained with this analysis can be summarized in the following points:

- If the reaction i and the reaction $j\neq i$ have no common chemical species, *i.e.*, when the reactions are uncoupled, the cross-terms shall vanish and $W(\boldsymbol{\zeta})$ is simplified. Furthermore, if the energy barrier is negligible for all reactions, then all terms are negative and the system converges to the equilibrium.
- When a chemical specie is a product and a reactant at the same time, or in other words, is an intermediate, the cross-terms have important contributions to the system's overall stability *even if no energy barrier is present*, *i.e.*, they can add positive terms to the entropy production found in $\mathbf{W}(\boldsymbol{\zeta})$, thus promoting complex behaviors. For instance, for a particular case with a reaction network of the form

$$\begin{aligned} r_1:&\quad E_1+E_2 \rightleftharpoons E_3\\ r_2:&\quad E_2+E_3 \rightleftharpoons E_4\end{aligned}$$

with an additional inert compound E_5 ($\omega=2$, $n=5$), it is straightforward to define

$$\mathbf{A}=\begin{pmatrix}1&0\\1&1\\0&1\\0&0\\0&0\end{pmatrix},\qquad \mathbf{B}=\begin{pmatrix}0&0\\0&0\\1&0\\0&1\\0&0\end{pmatrix},\qquad \text{and}\qquad \Gamma=\begin{pmatrix}-1&0\\-1&-1\\1&-1\\0&1\\0&0\end{pmatrix}.$$

Thus, the matrices necessary to compute $\mathbf{W}(\boldsymbol{\zeta})$

$$\boldsymbol{\Gamma}^{\mathrm{T}}\mathbf{u}\mathbf{u}^{\mathrm{T}}\boldsymbol{\Gamma} = \begin{pmatrix} \left(\Delta_{r,1}u\right)^2 & \left(\Delta_{r,1}u\right)\left(\Delta_{r,2}u\right) \\ \left(\Delta_{r,2}u\right)\left(\Delta_{r,1}u\right) & \left(\Delta_{r,2}u\right)^2 \end{pmatrix},$$

$$\mathbf{A}^{\mathrm{T}}[\mathrm{diag}\,(\mathbf{N})]^{-1}\mathbf{A} - \mathbf{B}^{\mathrm{T}}[\mathrm{diag}\,(\mathbf{N})]^{-1}\mathbf{A} = \begin{pmatrix} \dfrac{1}{N_1}+\dfrac{1}{N_2} & \dfrac{1}{N_2}-\dfrac{1}{N_3} \\ \dfrac{1}{N_2} & \dfrac{1}{N_2}+\dfrac{1}{N_3} \end{pmatrix},$$

$$\mathbf{B}^{\mathrm{T}}[\mathrm{diag}\,(\mathbf{N})]^{-1}\mathbf{B} - \mathbf{A}^{\mathrm{T}}[\mathrm{diag}\,(\mathbf{N})]^{-1}\mathbf{B} = \begin{pmatrix} \dfrac{1}{N_3} & 0 \\ -\dfrac{1}{N_3} & \dfrac{1}{N_4} \end{pmatrix},$$

and

$$\boldsymbol{\Gamma}^{\mathrm{T}}\mathbf{u}\mathbf{E}_{a0}^{\mathrm{T}}\mathrm{diag}\,(\boldsymbol{\mathcal{A}}) = \begin{pmatrix} \left(\Delta_{r,1}u\right)E_{a0,1}\mathcal{A}_1 & \left(\Delta_{r,1}u\right)E_{a0,2}\mathcal{A}_2 \\ \left(\Delta_{r,2}u\right)E_{a0,1}\mathcal{A}_1 & \left(\Delta_{r,2}u\right)E_{a0,2}\mathcal{A}_2 \end{pmatrix}$$

contain the interactions between reaction 1 and reaction 2.

Often the concentration of intermediates is small [38], and how they can move away system from the equilibrium is visible in the second and third terms in Eq. (48). Note that the magnitude of the cross-terms can be considerably increased due to $[\mathrm{diag}\,(\mathbf{N})]^{-1}$ when their concentration is small.

6. Conclusion

Under the MNET framework it is possible to model conservative phenomena in chemical reactions, making the effect of the mesoscopic conservative elements observable at the macroscopic scale, particularly in the dynamics of Σ, as the conservative elements "pull" the system away from the thermodynamic equilibrium, resulting in damped dissipation. Since mesoscopic dynamics are considerably faster than their macroscopic counterparts, the overall macroscopic process appears to be purely dissipative according to the formulation proposed in Section 4 for the entropy production. Nonetheless, including $E_a(\gamma)$ in the mesoscopic chemical potential results in a transient conservative–dissipative behavior, which affects the dynamics of the macroscopic state variables due to the added nonlinearities through $\left(\nabla_{\zeta}\mathbf{r}(\boldsymbol{\zeta})\right)M^{\mathrm{T}}\boldsymbol{\zeta}$, which can result in an increase in Σ when the system is far from the thermodynamic equilibrium.

When the energy barrier is present in a single reaction system, Σ can no longer be considered as a global Lyapunov function if the system is far from equilibrium, because the sign of $\kappa(\boldsymbol{\zeta}) - \chi(\boldsymbol{\zeta})$ cannot be known in advance and $\dot{\Sigma}$ can pass through zero when the driving forces are not, *i.e.*, when $-\mathcal{A}/T \neq 0$. The expression for the entropy production can give insights on how complex behaviors such as oscillations can be related with conservative phenomena when the system is far from equilibrium even if these conservative phenomena takes place at smaller scales, something that cannot be inferred by inspecting free energy dissipation alone.

The behavior shown in the first case study can become more complex when several simultaneous reactions are taking place, especially when a chemical specie participates in two or more reactions. This can be observed in the coupled terms in $\nabla\Sigma$, thus showing how the stoichiometry can add instabilities that promote complex behaviors found in some known reaction networks.

Although isolated reacting systems shall eventually reach the thermodynamic equilibrium, the transient behavior is quite important since it can explain how certain fixed points are favored in open systems, since the entropy production tends to reach extremals [39]. The authors believe that it is possible to generate oscillations in the state variables by adding interactions with several surroundings.

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References

[1] M.A. Zárate-Navarro, J.P. García-Sandoval, The effect of conservative and dissipative elements in chemical reactions, in: 2nd IFAC Workshop on Thermodynamic Foundation of Mathematical Systems Theory, Elsevier, Vigo, Spain, 2016. http://dx.doi.org/10.1016/j.ifacol.2016.10.742.
[2] J. Bao, P.L. Lee, Process Control: The Passive Systems Approach, Springer Science & Business Media, 2007.
[3] H. Hoang, F. Couenne, C. Jallut, Y. Le Gorrec, The port Hamiltonian approach to modeling and control of continuous stirred tank reactors, J. Process Control 21 (10) (2011) 1449–1458. http://dx.doi.org/10.1016/j.jprocont.2011.06.014.
[4] H. Ramírez, B. Maschke, D. Sbarbaro, Irreversible port-Hamiltonian systems: A general formulation of irreversible processes with application to the CSTR, Chem. Eng. Sci. 89 (2013) 223–234. http://dx.doi.org/10.1016/j.ces.2012.12.002.

[5] A. Favache, D. Dochain, Power-shaping control of reaction systems: The CSTR case, Automatica 46 (11) (2010) 1877–1883. http://dx.doi.org/10.1016/j.automatica.2010.07.011.
[6] N.H. Hoang, D. Dochain, N. Hudon, A thermodynamic approach towards Lyapunov based control of reaction rate, in: IFAC World Congress 2014, vol. 47, Elsevier, 2014, pp. 9117–9122.
[7] J.P. García-Sandoval, V. González-Álvarez, C. Calderón, Stability analysis and passivity properties for a class of chemical reactors: Internal entropy production approach, Comput. Chem. Eng. 75 (2015) 184–195. http://dx.doi.org/10.1016/j.compchemeng.2015.01.021.
[8] N. Hudon, D. Dochain, N.H. Hoang, J.P. Garcia-Sandoval, Potential-based analysis of closed reacting systems, IFAC-Papers OnLine 48 (8) (2015) 1065–1069. http://dx.doi.org/10.1016/j.ifacol.2015.09.109.
[9] I. Otero-Muras, G. Szederkényi, A.A. Alonso, K.M. Hangos, Local dissipative Hamiltonian description of reversible reaction networks, Systems Control Lett. 57 (7) (2008) 554–560. http://dx.doi.org/10.1016/j.sysconle.2007.12.003.
[10] K. Banerjee, K. Bhattacharyya, States with identical steady dissipation rate in reaction networks: A non-equilibrium thermodynamic insight in enzyme efficiency, Chem. Phys. 438 (2014) 1–6. http://dx.doi.org/10.1016/j.chemphys.2014.04.007.
[11] G. Nicolis, I. Prigogine, Self-Organization in Nonequilibrium Systems, Wiley, New York, 1977.
[12] N.G. Van Kampen, Stochastic Processes in Physics and Chemistry, vol. 1, Elsevier, 1992.
[13] D. Jou, J. Casas-Vázquez, G. Lebon, Extended irreversible thermodynamics, in: Extended Irreversible Thermodynamics, Springer, 1996, pp. 41–74.
[14] M. Grmela, Fluctuations in extended mass-action-law dynamics, Physica D 241 (10) (2012) 976–986. http://dx.doi.org/10.1016/j.physd.2012.02.008.
[15] V. Klika, M. Grmela, Coupling between chemical kinetics and mechanics that is both nonlinear and compatible with thermodynamics, Phys. Rev. E 87 (1) (2013) 012141. http://dx.doi.org/10.1103/PhysRevE.87.012141.
[16] I. Pagonabarraga, A. Pérez-Madrid, J. Rubi, Fluctuating hydrodynamics approach to chemical reactions, Physica A 237 (1) (1997) 205–219. http://dx.doi.org/10.1016/S0378-4371(96)00377-9.
[17] D. Bedeaux, S. Kjelstrup, J.V. Sengers, Experimental Thermodynamics Volume X: Non-Equilibrium Thermodynamics with Applications, vol. 10, Royal Society of Chemistry, 2015.
[18] S.R. De Groot, P. Mazur, Non-Equilibrium Thermodynamics, Dover Books, New York, 2013.
[19] D. Reguera, J.M. Rubí, J. Vilar, The mesoscopic dynamics of thermodynamic systems, J. Phys. Chem. B 109 (46) (2005) 21502–21515. http://dx.doi.org/10.1021/jp052904i.
[20] S. Kjelstrup, D. Bedeaux, E. Johannessen, J. Gross, Non-Equilibrium Thermodynamics for Engineers, World Scientific, 2010.
[21] J.P. García-Sandoval, N. Hudon, D. Dochain, V. González-Álvarez, Stability analysis and passivity properties of a class of thermodynamic processes: An internal entropy production approach, Chem. Eng. Sci. 139 (2016) 261–272. http://dx.doi.org/10.1016/j.ces.2015.07.039.
[22] J.C. Willems, Dissipative dynamical systems part i: General theory, Arch. Ration. Mech. Anal. 45 (5) (1972) 321–351.
[23] H. Khalil, Nonlinear Systems, third ed., Prentice Hall, 2002.
[24] Y. Demirel, Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical, Chemical and Biological Systems, third ed., Elsevier, 2014.
[25] G. Lebon, D. Jou, J. Casas-Vázquez, Understanding Non-Equilibrium Thermodynamics, Springer, 2008.
[26] D. Kondepudi, I. Prigogine, Modern Thermodynamics: From Heat Engines to Dissipative Structures, John Wiley & Sons, 2014.
[27] L. Onsager, Reciprocal relations in irreversible processes. I, Phys. Rev. 37 (4) (1931) 405. http://dx.doi.org/10.1103/PhysRev.37.405.
[28] I. Levine, Physical Chemistry, McGraw Hill, 2009.
[29] A. Cooksy, Physical Chemistry: Thermodynamics, Statistical Mechanics, and Kinetics, Pearson Higher Ed, 2013.
[30] G. Hvistendahl, D.H. Williams, Partitioning of reverse activation energy between kinetic and internal energy in reactions of some simple organic ions, J. Chem. Soc. Perkin Trans. 2 (9) (1975) 881–885. http://dx.doi.org/10.1039/P29750000881.
[31] R. Ortega, A. Van Der Schaft, B. Maschke, G. Escobar, Interconnection and damping assignment passivity-based control of port-controlled Hamiltonian systems, Automatica 38 (4) (2002) 585–596. http://dx.doi.org/10.1016/S0005-1098(01)00278-3.
[32] H.A. Kramers, Brownian motion in a field of force and the diffusion model of chemical reactions, Physica 7 (4) (1940) 284–304. http://dx.doi.org/10.1016/S0031-8914(40)90098-2.
[33] H. Eyring, E.M. Eyring, Modern Chemical Kinetics, Reinhold Publishing Corporation, 1963.
[34] A. Gorban, I. Karlin, V. Zmievskii, S. Dymova, Reduced description in the reaction kinetics, Physica A 275 (3) (2000) 361–379. http://dx.doi.org/10.1016/S0378-4371(99)00402-1.
[35] A. Isidori, Nonlinear Control Systems, third ed., Communications & Control Engineering, Springer-Verlag, London, 2000.
[36] G.R. Gavalas, Nonlinear Differential Equations of Chemically Reacting Systems, first ed., in: Springer Tracts in Natural Philosophy, vol. 17, Springer-Verlag, Berlin, Heidelberg, 1968.
[37] J. Manion, R. Huie, R. Levin, D. Burgess, V. Orkin, W. Tsang, W. McGivern, J. Hudgens, V. Knyazev, D. Atkinson, E. Chai, A. Tereza, C. Lin, T. Allison, W. Mallard, F. Westley, J. Herron, R. Hampson, D. Frizzell, NIST Chemical Kinetics Database, version 70 (web version), release 168, data version 201512 Edition, NIST Standard Reference Database 17, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320, 2015.
[38] I.R. Epstein, J.A. Pojman, An Introduction to Nonlinear Chemical Dynamics, Oxford Univ. Press, 1998.
[39] L. Martyushev, V. Seleznev, Maximum entropy production principle in physics, chemistry and biology, Phys. Rep. 426 (1) (2006) 1–45. http://dx.doi.org/10.1016/j.physrep.2005.12.001.