EXPONENTIAL TIME DECAY OF SOLUTIONS TO REACTION-CROSS-DIFFUSION SYSTEMS OF MAXWELL–STEFAN TYPE

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Abstract. The large-time asymptotics of weak solutions to Maxwell–Stefan diffusion systems for chemically reacting fluids with different molar masses and reversible reactions are investigated. The diffusion matrix of the system is generally neither symmetric nor positive definite, but the equations admit a formal gradient-flow structure which provides entropy (free energy) estimates. The main result is the exponential decay to the unique equilibrium with a rate that is constructive up to a finite-dimensional inequality. The key elements of the proof are the existence of a unique detailed-balanced equilibrium and the derivation of an inequality relating the entropy and the entropy production. The main difficulty comes from the fact that the reactions are represented by molar fractions while the conservation laws hold for the concentrations. The idea is to enlarge the space of n partial concentrations by adding the total concentration, viewed as an independent variable, thus working with $n+1$ variables. Further results concern the existence of global bounded weak solutions to the parabolic system and an extension of the results to complex-balanced systems.

Contents

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1. Introduction

The analysis of the large-time behavior of dynamical networks is important to understand their stability properties. Of particular interest are reversible chemical reactions interacting with diffusion. While there is a vast literature on the large-time asymptotics of reaction-diffusion systems, much less results are available for reaction systems with cross-diffusion terms. Such systems arise naturally in multicomponent fluid modeling and population dynamics [32]. In this paper, we prove the exponential decay of solutions to reaction-cross-diffusion systems of Maxwell–Stefan form by combining recent techniques for cross-diffusion systems [31] and reaction-diffusion equations [20]. The main feature of our result is that the decay rate is constructive up to a finite-dimensional inequality and that the result holds for detailed-balanced or complex-balanced systems.

1.1. **Model equations.** We consider a fluid consisting of n constituents A_i with mass densities $\rho_i(z,t)$ and molar masses M_i, which are diffusing according to the diffusive fluxes $\boldsymbol{j}_i(z,t)$ and reacting in the following reversible reactions,

$$\alpha_1^a A_1 + \cdots + \alpha_n^a A_n \leftrightharpoons \beta_1^a A_1 + \cdots + \beta_n^a A_n \quad \text{for } a = 1,\ldots,N,$$

where α_i^a and β_i^a are the stoichiometric coefficients. The evolution of the fluid is assumed to be governed by partial mass balances with Maxwell–Stefan relations for the diffusive fluxes,

$$\partial_t\rho_i + \operatorname{div}\boldsymbol{j}_i = r_i(\boldsymbol{x}), \quad \nabla x_i = -\sum_{j=1}^n \frac{\rho_j\boldsymbol{j}_i - \rho_i\boldsymbol{j}_j}{c^2 M_i M_j D_{ij}}, \quad i = 1,\ldots,n, \tag{1}$$

where $x_i = c_i/c$ are the molar fractions, $c_i = \rho_i/M_i$ the partial concentrations, M_i the molar masses, $c = \sum_{i=1}^n c_i$ the total concentration, and $D_{ij} = D_{ji} > 0$ are the diffusivities. The physical quantities are summarized in Table 1. The reactions are described by the mass production terms r_i depending on $\boldsymbol{x} = (x_1, \ldots, x_n)$ using mass-action kinetics,

$$r_i(\boldsymbol{x}) = M_i \sum_{a=1}^{N} (\beta_i^a - \alpha_i^a)(k_f^a \boldsymbol{x}^{\boldsymbol{\alpha^a}} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta^a}}) \quad \text{with } \boldsymbol{x}^{\boldsymbol{\alpha^a}} := \prod_{i=1}^{n} x_i^{\alpha_i^a}, \tag{2}$$

where $k_f^a > 0$ and $k_b^a > 0$ are the forward and backward reaction rate constants, respectively, and $\boldsymbol{\alpha}^a = (\alpha_1^a, \ldots, \alpha_n^a)$ and $\boldsymbol{\beta}^a = (\beta_1^a, \ldots, \beta_n^a)$ with α_i^a, $\beta_i^a \in \{0\} \cup [1, \infty)$ are the vectors of the stoichiometric coefficients.

ρ_i	: partial mass density of the ith species
$\rho = \sum_{i=1}^n \rho_i$	: total mass density
$\boldsymbol{j}_i$	: partial particle flux of the ith species
M_i	: molar mass of the ith species
$c_i = \rho_i / M_i$	: partial concentration of the ith species
$c = \sum_{i=1}^n c_i$	: total concentration
$x_i = c_i / c$	: molar fraction

TABLE 1. Overview of the physical quantities.

Equations (1) are solved in the bounded domain $\Omega \subset \mathbb{R}^d$ $(d \geqslant 1)$ subject to the no-flux boundary and initial conditions

$$\boldsymbol{j}_i \cdot \nu = 0 \text{ on } \partial\Omega, \quad \rho_i(\cdot, 0) = \rho_i^0 \quad \text{in } \Omega,\ i = 1, \ldots, n. \tag{3}$$

To simplify, we assume that Ω has unit measure, i.e. $|\Omega| = 1$.

System (1)-(2) models a multicomponent fluid in an isothermal regime with vanishing barycentric velocity. Equations (1) for ∇x_i can be derived from the Boltzmann equations for mixtures in the diffusive limit and with well-prepared initial conditions [6, 29, 30] or from the reduced force balances with the partial momentum productions being proportional to the partial velocity differences [4, Section 14].

We assume that the total mass is conserved and that the mixture is at rest, i.e., $\sum_{i=1}^n \rho_i = 1$ and $\sum_{i=1}^n \boldsymbol{j}_i = 0$. This implies that

$$\sum_{i=1}^{n} r_i(\boldsymbol{x}) = 0 \quad \text{for all } \boldsymbol{x} = (x_1, \ldots, x_n) \in \mathbb{R}_+^n, \tag{4}$$

where $\mathbb{R}_+ = (0, \infty)$. Furthermore, we assume that the system of reactions satisfies a detailed-balanced condition, meaning that there exists a positive homogeneous equilibrium $\boldsymbol{x}_\infty \in \mathbb{R}_+^n$ such that

$$k_f^a \boldsymbol{x}_\infty^{\boldsymbol{\alpha}^a} = k_b^a \boldsymbol{x}_\infty^{\boldsymbol{\beta}^a} \quad \text{for all } a = 1, \ldots, N. \tag{5}$$

Roughly speaking, a system is under detailed balance if any forward reaction is balanced by the corresponding backward reaction at equilibrium. Condition (5) does not give a unique but instead a manifold of detailed-balanced equilibria,

$$\mathcal{E} = \left\{ \boldsymbol{x}_\infty \in \mathbb{R}^n_+ : \ k_f^a \boldsymbol{x}_\infty^{\boldsymbol{\alpha}^a} = k_b^a \boldsymbol{x}_\infty^{\boldsymbol{\beta}^a} \quad \text{for all } a = 1, \ldots, N \right\}. \tag{6}$$

To uniquely identify the detailed-balanced equilibrium, we need to take into account the conservation laws (meaning that certain linear combinations of the concentrations are constant in time). This is discussed in detail below. We are also able to consider complex-balanced systems; see Section 5.

The aim of this paper is to prove that under these conditions, there exists a unique positive detailed-balanced (or complex-balanced) equilibrium $\boldsymbol{x}_\infty = (x_{1\infty}, \ldots, x_{n\infty}) \in \mathbb{R}^n_+$ such that

$$\sum_{i=1}^n \|x_i(t) - x_{i\infty}\|_{L^p(\Omega)} \leqslant C(\boldsymbol{x}^0, \boldsymbol{x}_\infty) e^{-\lambda t/(2p)}, \quad t > 0, \ p \geqslant 1,$$

where $\boldsymbol{x}^0 = \boldsymbol{x}(0)$ and the constant $\lambda > 0$ is constructive up to a finite-dimensional inequality. Before we make this result precise, we review the state of the art and explain the main difficulties and key ideas.

1.2. **State of the art.** The research of the large-time asymptotics of general reaction-diffusion systems with diagonal diffusion, modeling chemical reactions, has experienced a dramatic scientific progress in recent years. One reason for this progress is due to new developments of so-called entropy methods. Classical methods include linearized stability techniques, spectral theory, invariant region arguments, and Lyapunov stability; see, e.g., [10, 21]. The entropy method is a genuinely nonlinear approach without using any kind of linearization, it is rather robust against model variations, and it is able to provide explicitly computable decay rates. The first related works date back to the 1980s [24, 25]. The obtained results are restricted to two space dimensions and do not provide explicit estimates, since the proofs are based on contradiction arguments. First applications of the entropy method that provide explicit rates and constants were concerned with particular cases, like two-component systems [12], four-component systems [14], or multicomponent linear systems [15]. Later, nonlinear reaction networks with an arbitrary number of chemical substances were considered [19, 35]. Exponential convergence of close-to-equilibrium solutions to quadratic reaction-diffusion systems with detailed balance was shown in [7]. Reaction-diffusion systems without detailed balance [18] and with complex balance [13, 36, 42] were also thoroughly investigated. The convergence to equilibrium was proven for rather general solution concepts, like very weak solutions [38] and renormalized solutions [20].

The large-time behavior of solutions to cross-diffusion systems is less studied in the literature. The convergence to equilibrium was shown for the Shigesada–Kawasaki–Teramoto population model with Lotka–Volterra terms in [40, 44] without any rate and in [8] without reaction terms. The exponential decay of solutions to volume-filling population systems, again without reaction terms, was proved in [45].

A number of articles is concerned with the large-time asymptotics in Maxwell–Stefan systems. For global existence results on these systems, we refer to [26, 33, 34]. In [33], the exponential decay to the homogeneous state state is shown with vanishing reaction rates and same molar masses. The result was generalized to different molar masses in

[9], but still without reaction terms. The convergence to equilibrium was proved in [22, Theorem 9.7.4] and [26, Theorem 4.3] under the condition that the initial datum is close to the equilibrium state. The work [26] also addresses the exponential convergence to a homogeneous equilibrium assuming (i) global existence of strong solutions and (ii) uniform-in-time strict positivity of the solutions (see Prop. 4.4 therein). A similar result, but for two-phase systems, was proved in [5]. The novelty in our paper is that we provide also a global existence proof (which avoids assumption (i)) and that we replace the strong assumption (ii) by a natural condition on the reactions, namely that there exist no equilibria on $\partial\mathbb{R}^n_+$. We note that there exists a large class of chemical reaction networks, called *concordant networks*, which possess no boundary equilibria [41, Theorem 2.8(ii)].

1.3. **Key ideas.** The analysis of the Maxwell–Stefan equations (1) is rather delicate. The first difficulty is that the fluxes are not given as linear combinations of the gradients of the mass fractions, which makes it necessary to invert the flux-gradient relations in (1). However, summing the equations for ∇x_i in (1) for $i = 1, \ldots, n$, we see that the Maxwell–Stefan equations are linear dependent, and we need to invert them on a subspace [3]. The idea is to work with the $n-1$ variables $\boldsymbol{\rho}' = (\rho_1, \ldots, \rho_{n-1})^\top$ by setting $\rho_n = 1 - \sum_{i=1}^{n-1} \rho_i$, i.e., the mass density of the last component (often the solvent) is computed from the other mass densities. Then there exists a diffusion matrix $\mathbb{A}(\boldsymbol{\rho}') \in \mathbb{R}^{(n-1)\times(n-1)}$ such that system (1) can be written as

$$\partial_t \boldsymbol{\rho}' - \operatorname{div}(\mathbb{A}(\boldsymbol{\rho}')\nabla \boldsymbol{x}') = \boldsymbol{r}'(\boldsymbol{x}), \tag{7}$$

where $\boldsymbol{x}' = (x_1, \ldots, x_{n-1})^\top$ and $\boldsymbol{r}' = (r_1, \ldots, r_{n-1})^\top$. The matrix $\mathbb{A}(\boldsymbol{\rho}')$ is generally neither symmetric nor positive definite. However, equations (7) exhibit a formal gradient-flow structure [33]. This means the following: We introduce the so-called (relative) entropy density

$$h(\boldsymbol{\rho}') = c\sum_{i=1}^n x_i \ln\frac{x_i}{x_{i\infty}}, \quad \text{where } \rho_n = 1 - \sum_{i=1}^{n-1}\rho_i, \tag{8}$$

and the entropy variable $\boldsymbol{w} = (w_1, \ldots, w_{n-1})^\top$ with $w_i = \partial h/\partial\rho_i$. Here, $\boldsymbol{x}_\infty \in \mathcal{E}$ is an arbitrary detailed-balanced equilibrium. We associate to the entropy density the relative entropy (or free energy)

$$E[\boldsymbol{x}|\boldsymbol{x}_\infty] = \int_\Omega h(\boldsymbol{\rho}')dz = \sum_{i=1}^n \int_\Omega c x_i \ln\frac{x_i}{x_{i\infty}} dz. \tag{9}$$

Denoting by $h''(\boldsymbol{\rho}')$ the Hessian of h with respect to $\boldsymbol{\rho}'$, equation (7) is equivalent to

$$\partial_t \boldsymbol{\rho}' - \operatorname{div}(\mathbb{B}(\boldsymbol{w})\nabla \boldsymbol{w}) = \boldsymbol{r}'(\boldsymbol{x}), \tag{10}$$

where $\mathbb{B}(\boldsymbol{w}) = \mathbb{A}(\boldsymbol{\rho}')h''(\boldsymbol{\rho}')^{-1}$ is symmetric and positive definite [9, Lemma 10 (iv)] and $\boldsymbol{\rho}'$ and $\boldsymbol{x}$ are functions of $\boldsymbol{w}$. The elliptic operator can be formulated as $\mathbb{K}\operatorname{grad} h(\boldsymbol{\rho}')$, where $\mathbb{K}\xi = \operatorname{div}(\mathbb{B}\nabla\xi)$ is the Onsager operator and grad is the functional derivative. This formulation motivates the notion “gradient-flow structure”.

The second difficulty comes from the fact that the cross-diffusion coupling prevents the use of standard tools like maximum principles and regularity theory. In particular, it is not clear how to prove lower and upper bounds for the mass densities or molar fractions. Surprisingly, this problem can be also solved by the transformation to entropy variables. Indeed, the mapping $(0,1)^{n-1}\to\mathbb{R}^{n-1}$, $\boldsymbol{\rho}'\mapsto\boldsymbol{w}$, can be inverted, and the image $\boldsymbol{\rho}'(\boldsymbol{w})$ lies in $(0,1)^{n-1}$ and satisfies $1-\sum_{i=1}^{n-1}\rho_i<1$. If all molar masses are equal, $M=M_i$, the inverse function can be written explicitly as $\rho_i(\boldsymbol{w})=\exp(Mw_i)(1+\sum_{j=1}^{n-1}\exp(Mw_j))^{-1}$; for the general case see Lemma 4 below. This yields the positivity and L^∞ bounds for ρ_i without the use of a maximum principle. To make this argument rigorous, we first need to solve (10) for $\boldsymbol{w}$ and then to conclude that $\boldsymbol{\rho}'=\boldsymbol{\rho}'(\boldsymbol{w})$ solves (1).

Summarizing, the entropy helps us to "symmetrize" system (1) and to derive L^∞ bounds. There is a further benefit: The entropy is a Lyapunov functional along solutions to the detailed-balanced system (1). Indeed, a formal computation shows the following relation (a weaker discrete version is made rigorous in the proof of Theorem 3),

$$\frac{d}{dt}E[\boldsymbol{x}|\boldsymbol{x}_\infty]+D[\boldsymbol{x}]=0,\quad t>0, \tag{11}$$

where the entropy production

$$D[\boldsymbol{x}]=\sum_{i,j=1}^{n-1}\int_\Omega B_{ij}(\boldsymbol{w})\nabla w_i\cdot\nabla w_j dz+\sum_{a=1}^{N}\int_\Omega(k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a})\ln\frac{k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a}}dz \tag{12}$$

is nonnegative (due to Lemmas 5 and 6). Here, B_{ij} are the coefficients of the matrix $\mathbb{B}$. Exponential decay follows if the entropy entropy-production inequality

$$D[\boldsymbol{x}]\geqslant\lambda E[\boldsymbol{x}|\boldsymbol{x}_\infty] \tag{13}$$

holds for all suitable functions $\boldsymbol{x}$ and for some $\lambda>0$. Note that this functional inequality does not hold for all detailed-balanced equilibria, but only for those who satisfy certain conservation laws. The existence and uniqueness of such equilibria is proved in Theorem 10. Inserting inequality (13) into (11) yields

$$\frac{d}{dt}E[\boldsymbol{x}|\boldsymbol{x}_\infty]+\lambda E[\boldsymbol{x}|\boldsymbol{x}_\infty]\leqslant 0,\quad t>0,$$

and Gronwall's inequality allows us to conclude that

$$E[\boldsymbol{x}(t)|\boldsymbol{x}_\infty]\leqslant E[\boldsymbol{x}(0)|\boldsymbol{x}_\infty]e^{-\lambda t},\quad t>0.$$

By a variant of the Csiszár–Kullback–Pinsker inequality (Lemma 17), this gives exponential decay in the L^1 norm with rate $\lambda/2$ and, by interpolation, in the L^p norm with rate $\lambda/(2p)$ for all $1\leqslant p<\infty$. An important feature of this result is that the constant λ is constructive up to a finite-dimensional inequality.

The cornerstone of the convergence to equilibrium is to prove inequality (13). In comparison to previous results for reaction-diffusion systems, e.g. [19, 35], the difference here is that the reactions are defined in terms of molar fractions, while the conservation laws are written in terms of concentrations. This difference causes the main difficulty in proving (13), except in very special cases, e.g., when all molar masses are equal (in this case, the molar fraction and concentration are proportional) or in case of equal homogeneities (see Section 3.4). Naturally, one could express the molar fractions by the concentrations, i.e. $x_i = c_i/(\sum_{i=1}^n c_i)$, but this extremely complicates the formulation of the entropy production $D[\boldsymbol{x}]$, which in turn makes the analysis of (13) inaccessible. The key idea here is to introduce the total concentration $c = \sum_{i=1}^n c_i$ as an independent variable and to rewrite $D[\boldsymbol{x}]$ in terms of $x_i = c_i/c$. This, in combination with an estimate for $E[\boldsymbol{x}|\boldsymbol{x}_\infty]$ in terms of c_i and c, allows us to adapt the ideas from previous works on reaction-diffusion systems to finally obtain the desired inequality (13).

1.4. **Main results.** Our main result is the exponential convergence to equilibrium. For this, we need to show some intermediate results. The existence of solutions to (1), (3) was shown in [9] without reaction terms. Therefore, we prove the global existence of bounded weak solutions to (1), (3) with reaction terms (2). The proof follows that one in [9] but the estimates related to the reaction terms are different. A key step is the proof of the monotonicity of $\boldsymbol{w} \mapsto \sum_{i=1}^{n-1} r_i(\boldsymbol{x})$; see Lemma 6.

Second, we derive the conservation laws satisfied by the solutions to (1) (Lemma 8) and prove the existence of a positive detailed-balanced equilibrium $\boldsymbol{x}_\infty$ satisfying (5) and the conservation laws (Theorem 10). The existence of unique equilibrium states for chemical reaction networks is well studied in the literature (see, e.g., [16]), but not in the present framework. One difficulty is the additional constraint $\sum_{i=1}^n x_i = 1$, which significantly complicates the analysis. The key idea for the existence of a unique detailed-balanced equilibrium is to analyze systems in the partial concentrations $c_1, \ldots, c_n$ *and* the total concentration c, considered as an independent variable. The increase of the dimension of the system from n to $n+1$ allows us to apply geometric arguments and a result of Feinberg [16] to achieve the claim.

Third, we prove the entropy entropy-production inequality (13) (Prop. 18 and 25). The proof follows basically from [20, Lemma 2.7] when the stoichiometric coefficients satisfy $\sum_{i=1}^n \alpha_i^a = \sum_{i=1}^n \beta_i^a$ for all $a = 1, \ldots, N$, since this property allows us to replace the molar fractions x_i by the concentrations c_i. If the property is not fulfilled, we work again in the augmented space of concentrations $(c_1, \ldots, c_n, c)$. One step of the proof (Lemma 21) requires the proof of an inequality whose constant is constructive only up to a finite-dimensional inequality. We believe that for concrete systems, this constant can be computed in a constructive way. We present such an example in Section 4.

Before stating the main theorem, we need some notation. Let

$$\mathbb{W} = (\boldsymbol{\beta}^a - \boldsymbol{\alpha}^a)_{a=1,\ldots,N} \in \mathbb{R}^{n\times N},$$

be the Wegscheider matrix (or stoichiometric coefficients matrix) and set $m = \dim\ker(\mathbb{W}^\top) > 0$. We choose a matrix $\mathbb{Q} \in \mathbb{R}^{m\times n}$ whose rows form a basis of $\ker(\mathbb{W}^\top)$. Let $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ be the initial mass vector, which depends on $\boldsymbol{c}^0$ (see Lemma 8) and let $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ be a row vector satisfying $\boldsymbol{\zeta}\mathbb{Q} = (M_1, \ldots, M_n)$ and $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. We show in Lemma 9 that such a vector $\boldsymbol{\zeta}$ always exists. Its appearance comes from the constraint $\sum_{i=1}^n x_i = 1$; such a vector is not needed in reaction-diffusion systems like in [20]. Given $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ such that $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$, we prove in Section 3.2 that there exists a unique positive *detailed-balanced* *equilibrium* $\boldsymbol{x}_\infty \in \mathcal{E}$ satisfying

$$\mathbb{Q}\boldsymbol{c}_\infty = \boldsymbol{M}^0, \quad \sum_{i=1}^n x_{i\infty} = 1, \tag{14}$$

where the components of $\boldsymbol{c}_\infty$ are given by $c_{i\infty} = x_{i\infty}/\sum_{i=1}^n M_i x_{i\infty}$. The first expression in (14) are the conservation laws, while the second one is the normalization condition.

Note that besides the unique positive detailed-balanced equilibrium (for a fixed initial mass vector), there could exist possibly infinitely many *boundary equilibria*, i.e. $\boldsymbol{x}^* \in \partial\mathcal{E}$ such that $\boldsymbol{x}^*$ solves (14). We need to exclude such equilibria. For a discussion of boundary equilibria and the Global Attractor Conjecture, we refer to Remark 14.

- (A1) Data: $\Omega \subset \mathbb{R}^d$ with $d \geqslant 1$ is a bounded domain with Lipschitz boundary, $T > 0$, and $D_{ij} = D_{ji} > 0$ for $i, j = 1, \ldots, n$, $i \neq j$.
- (A2) Detailed-balance condition: $\mathcal{E} \neq \varnothing$, where $\mathcal{E}$ is defined in (6).
- (A3) Initial condition: $\boldsymbol{\rho}^0 \in L^1(\Omega; \mathbb{R}^n)$ with $\rho_i^0 \geqslant 0$, $\sum_{i=1}^n \rho_i^0 = 1$, and the initial entropy is finite, $\int_\Omega h(\boldsymbol{\rho}^{0\prime})dz < \infty$, where h is defined in (8) with some $\boldsymbol{x}_\infty \in \mathcal{E}$.

The main result is as follows.

Theorem 1 (Convergence to equilibrium)**.** *Let Assumptions* (A1)-(A3) *hold. Let* $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ *be a positive initial mass vector satisfying* $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$*. Then*

(i) *There exists a global bounded weak solution* $\boldsymbol{\rho} = (\rho_1, \ldots, \rho_n)^\top$ *to* (1)-(2) *in the sense of Theorem 3 below.*

(ii) *There exists a unique* $\boldsymbol{x}_\infty \in \mathcal{E}$ *satisfying* (14)*, where the set of equilibria* $\mathcal{E}$ *is defined in* (6)*.*

(iii) *Assume in addition that the system* (1)-(2) *has no boundary equilibria. Then there exist constants* $C > 0$ *and* $\lambda > 0$*, which are constructive up to a finite-dimensional inequality, such that, if* $\boldsymbol{\rho}^0$ *satisfies additionally* $\mathbb{Q}\int_\Omega \boldsymbol{c}^0 dz = \boldsymbol{M}^0$*, the following exponential convergence to equilibrium holds:*

$$\sum_{i=1}^n \|x_i(t) - x_{i\infty}\|_{L^p(\Omega)} \leqslant Ce^{-\lambda t/(2p)}\big(E[\boldsymbol{x}^0|\boldsymbol{x}_\infty]\big)^{1/(2p)}, \quad t > 0,$$

where $1 \leqslant p < \infty$*,* $x_i = \rho_i/(cM_i)$ *with* $c = \sum_{i=1}^n \rho_i/M_i$*,* $E[\boldsymbol{x}|\boldsymbol{x}_\infty]$ *is the relative entropy defined in* (9)*,* $\boldsymbol{\rho}$ *is the solution constructed in* (i)*, and* $\boldsymbol{x}_\infty$ *is constructed in* (ii)*.*

Remark 2 (Complex balance)**.** We show in Theorem 10 that system (1) with the reaction terms (2) possesses a unique positive detailed-balance equilibrium. This means that we have assumed the reversibility of the reaction system. This assumption is rather strong, and it is well known in chemical reaction network theory that it can be significantly generalized to complex-balanced systems. Here, the balance is not assumed to hold for any elementary reaction step but only for the total in-flow and total out-flow of each chemical complex. We are able to extend our results to this situation as well, considering the reaction terms (54); see Theorem 32 in Section 5.

Clearly, any detailed-balanced equilibrium is also a complex-balanced equilibrium, and Theorem 1 is included in Theorem 32. However, to make the proofs as accessible as possible, we prefer to present the detailed-balanced case in full detail and sketch the extension to complex-balanced systems. □

The paper is organized as follows. Part (i) of Theorem 1 is proved in Section 2. In Section 3, the conservation laws are derived, the existence of a detailed-balanced equilibrium and the entropy entropy-production inequality (13) are proved, and the convergence result is shown. Section 4 is concerned with a specific example for which the constant in the entropy entropy-production inequality can be computed explicitly. The results are extended to complex-balanced systems in Section 5. Finally, we prove the technical Lemma 20 in the appendix.

1.5. **Notation.** We use the following notation:

- Bold letters indicate vectors in $\mathbb{R}^n$ (e.g. $\boldsymbol{c} = (c_1, \ldots, c_n)^\top$).
- Normal letters denote the sum of all the components of the corresponding letter in bold font (e.g. $c = \sum_{i=1}^n c_i$).
- Primed bold letters signify that the last component is removed from the original vector (e.g. $\boldsymbol{c}' = (c_1, \ldots, c_{n-1})^\top$).
- Overlined letters usually denote integration over Ω (e.g. $\overline{\boldsymbol{c}} = \int_\Omega \boldsymbol{c} dz$ or $\overline{c_i} = \int_\Omega c_i dz$).
- If $f : \mathbb{R} \to \mathbb{R}$ is a function and $\boldsymbol{c} \in \mathbb{R}^n$ a vector, the expression $f(\boldsymbol{c})$ denotes the vector $(f(c_1), \ldots, f(c_n))^\top$.
- Let $\boldsymbol{x}$, $\boldsymbol{\alpha} \in (0, \infty)^n$. The expression $\boldsymbol{x}^{\boldsymbol{\alpha}}$ equals the product $\prod_{i=1}^n x_i^{\alpha_i}$.
- Matrices are generally denoted by double-barred capital letters (e.g. $\mathbb{A} \in \mathbb{R}^{m \times n}$).

The inner product in $\mathbb{R}^n$ is denoted by $\langle \cdot, \cdot \rangle$, $|\Omega|$ is the measure of Ω, and we set $\mathbb{R}_+ = (0, \infty)$. In the estimates, $C > 0$ denotes a generic constant with values changing from line to line.

2. Global existence of weak solutions

We prove part (i) of Theorem 1. Throughout this section, we fix an arbitrary detailed-balanced equilibrium $\boldsymbol{x}_\infty \in \mathcal{E}$. Due to (A2), such a vector $\boldsymbol{x}_\infty$ always exists. The existence result is stated more precisely in the following theorem.

Theorem 3 (Global existence)**.** *Let Assumptions (A1)-(A3) hold. Then there exists a bounded weak solution $\boldsymbol{\rho} = (\rho_1, \ldots, \rho_n)^\top$ to (1)-(3) satisfying $\rho_i \geqslant 0$, $\sum_{i=1}^n \rho_i = 1$ in $\Omega \times (0, T)$ and*

$$\rho_i \in L^2(0, T; H^1(\Omega)), \ \partial_t \rho_i \in L^2(0, T; H^1(\Omega)'), \quad i = 1, \ldots, n,$$

i.e., for all $q_1, \ldots, q_{n-1} \in L^2(0, T; H^1(\Omega))$,

$$\sum_{i=1}^{n-1} \int_0^T \langle \partial_t \rho_i, q_i \rangle dt + \sum_{i,j=1}^{n-1} \int_0^T \int_\Omega A_{ij}(\boldsymbol{\rho}') \nabla x_i \cdot \nabla q_j dz dt = \sum_{i=1}^{n-1} \int_0^T \int_\Omega r_i(\boldsymbol{x}) q_i dz dt, \tag{15}$$

where $\boldsymbol{x} = (x_1, \ldots, x_n)^\top$, $x_i = \rho_i/(cM_i)$ for $i = 1, \ldots, n-1$, $x_n = 1 - \sum_{i=1}^{n-1} x_i$, $c = \sum_{i=1}^n \rho_i/M_i$, and $\mathbb{A} = (A_{ij})$ is the diffusion matrix in (7).

The proof is similar to that one given in [9]. Since in that paper, no reaction terms have been considered, we need to show how these terms can be controlled. First, we collect some results.

2.1. **Preliminary results.** A straightforward computation (see [9, Lemma 5]) shows that the entropy variables are given by

$$w_i = \frac{\partial h}{\partial \rho_i} = \frac{1}{M_i}\ln\frac{x_i}{x_{i\infty}} - \frac{1}{M_n}\ln\frac{x_n}{x_{n\infty}}, \quad i = 1,\ldots,n-1, \tag{16}$$

recalling h defined in (8). Given $\boldsymbol{\rho}' = (\rho_1,\ldots,\rho_{n-1})^\top$, this formula and the relation $x_i = \rho_i/(cM_i)$ allow us to compute $\boldsymbol{w} = (w_1,\ldots,w_{n-1})^\top$. The following lemma states that the mapping $\boldsymbol{\rho}' \mapsto \boldsymbol{w}$ can be inverted.

Lemma 4. *Let $\boldsymbol{w} = (w_1,\ldots,w_{n-1})^\top \in \mathbb{R}^{n-1}$ be given. Then there exists a unique vector $\boldsymbol{\rho}' = (\rho_1,\ldots,\ \rho_{n-1})^\top \in (0,1)^{n-1}$ satisfying $\sum_{i=1}^{n-1}\rho_i < 1$ such that (16) holds with $\rho_n = 1 - \sum_{i=1}^{n-1}\rho_i > 0$, $x_i = \rho_i/(cM_i)$ and $c = \sum_{i=1}^n \rho_i/M_i$. Moreover, the function $\boldsymbol{\rho}' : \mathbb{R}^{n-1} \to (0,1)^{n-1}$, $(w_1,\ldots,w_{n-1})^\top \mapsto \boldsymbol{\rho}'(w) = (\rho_1,\ldots,\rho_{n-1})^\top$ is bounded.*

Proof. First, we show that there exists a unique vector $(x_1,\ldots,x_{n-1})^\top \in (0,1)^{n-1}$ satisfying (16) with $x_n = 1 - \sum_{i=1}^{n-1} x_i > 0$ (see [9, Lemma 6]). Let $z_i := x_{i\infty}/x_{n\infty}^{M_i/M_n}$. The function

$$f(s) = \sum_{i=1}^{n-1} z_i(1-s)^{M_i/M_n}\exp(M_i w_i)$$

is strictly decreasing in $[0,1]$ and $0 = f(1) < f(s) < f(0) = \sum_{i=1}^{n-1}\exp(M_i w_i) z_i$. Thus, there exists a unique fixed point $s_0 \in (0,1)$ such that $f(s_0) = s_0$. Defining $x_i = z_i(1-s_0)^{M_i/M_n}\exp(M_i w_i)$ for $i = 1,\ldots,n-1$, we infer that $x_i > 0$, $\sum_{i=1}^{n-1} x_i = f(s_0) = s_0 < 1$, and (16) holds with $x_n := 1 - s_0$.

Next, let $(x_1,\ldots,x_{n-1})^\top \in (0,1)^{n-1}$ and $x_n := 1 - \sum_{i=1}^{n-1} x_i > 0$ be given and define $\rho_i = cM_i x_i$, where $c = 1/(\sum_{i=1}^n M_i x_i)$. Then $(\rho_1,\ldots,\rho_{n-1})^\top \in (0,1)^{n-1}$ is the unique vector satisfying $\rho_n = 1 - \sum_{i=1}^{n-1}\rho_i > 0$, $x_i = \rho_i/(cM_i)$ for $i = 1,\ldots,n-1$, and $c = \sum_{i=1}^n \rho_i/M_i$ [9, Lemma 7]. Finally, the result follows by combining the previous steps. □

Lemma 5. *Let $\boldsymbol{w} \in H^1(\Omega;\mathbb{R}^{n-1})$. Then there exists a constant $C_B > 0$, which only depends on D_{ij} and M_i, such that*

$$\int_\Omega \nabla\boldsymbol{w} : \mathbb{B}(\boldsymbol{w})\nabla\boldsymbol{w}\,dz \geqslant C_B\sum_{i=1}^n\int_\Omega |\nabla x_i^{1/2}|^2 dz,$$

where ":" means summation over both matrix indices.

We recall that $\mathbb{B}(w) = \mathbb{A}(\boldsymbol{\rho}')h''(\boldsymbol{\rho}')^{-1}$ and h'' is the Hessian of the entropy h defined in (8). Lemma 5 is proved in [9, Lemma 12]. It is shown in [9, Lemma 9] that $\mathbb{B}$ is symmetric and positive definite.

2.2. **Solution to an approximate problem.** Let $T > 0$, $M \in \mathbb{N}$, $\tau = T/M$, $k \in \{1, \ldots, M\}$, $\varepsilon > 0$, and $l \in \mathbb{N}$ with $l > d/2$. Then the embedding $H^l(\Omega) \hookrightarrow L^\infty(\Omega)$ is compact. Given $\boldsymbol{w}^{k-1} \in L^\infty(\Omega; \mathbb{R}^{n-1})$, we wish to find $\boldsymbol{w}^k \in H^l(\Omega; \mathbb{R}^{n-1})$ such that

$$\begin{aligned}&\frac{1}{\tau}\int_\Omega \big(\boldsymbol{\rho}'(\boldsymbol{w}^k) - \boldsymbol{\rho}'(\boldsymbol{w}^{k-1})\big) \cdot \boldsymbol{q} dz + \int_\Omega \nabla \boldsymbol{q} : \mathbb{B}(\boldsymbol{w}^k)\nabla \boldsymbol{w}^k dz \\ &\quad + \varepsilon \int_\Omega \bigg(\sum_{|\boldsymbol{\alpha}|=l} D^{\boldsymbol{\alpha}} \boldsymbol{w}^k : D^{\boldsymbol{\alpha}} \boldsymbol{q} + \boldsymbol{w}^k \cdot \boldsymbol{q} \bigg) dz = \int_\Omega \boldsymbol{r}'(\boldsymbol{x}^k) \cdot \boldsymbol{q} dz, \end{aligned} \tag{17}$$

for all $\boldsymbol{q} \in H^l(\Omega; \mathbb{R}^{n-1})$, where $\boldsymbol{r}' = (r_1, \ldots, r_{n-1})^\top$, $x_i^k = \rho_i(\boldsymbol{w}^k)/(cM_i)$, and $\boldsymbol{\rho}'(\boldsymbol{w}^k)$ is defined in Lemma 4. Moreover, $\boldsymbol{\alpha} = (\alpha_1, \ldots, \alpha_d) \in \mathbb{N}_0^d$ is a multi-index of order $|\boldsymbol{\alpha}| = \alpha_1 + \cdots + \alpha_d = l$ and $D^{\boldsymbol{\alpha}} = \partial^{|\boldsymbol{\alpha}|}/(\partial z_1^{\alpha_1} \cdots \partial z_d^{\alpha_d})$ is a partial derivative of order l. The regularization with the lth-order derivative terms is needed since the matrix $\mathbb{B}$ is not uniformly positive definite. As $\boldsymbol{\rho}'$ is a bounded function of $\boldsymbol{w}$, we can apply the boundedness-by-entropy method of [31] or [9, Section 3.1] to deduce the existence of a weak solution $\boldsymbol{w}^k \in H^l(\Omega; \mathbb{R}^{n-1})$ to (17).

2.3. **Uniform estimates.** The crucial step is to derive some a priori estimates. The idea is to employ the test function $\boldsymbol{q} = \boldsymbol{w}^k$ in (17) and to proceed as in the proof of Lemma 14 of [9]. The reaction terms have no influence as the following lemma shows.

Lemma 6. *It holds that*

$$\boldsymbol{r}'(\boldsymbol{x}^k) \cdot \boldsymbol{w}^k = \sum_{i=1}^{n-1} r_i(\boldsymbol{x}^k) w_i^k \leqslant 0.$$

Proof. Let $\boldsymbol{x} = \boldsymbol{x}^k$ and $\boldsymbol{w} = \boldsymbol{w}^k$ to simplify. We deduce from (16) and total mass conservation (4) that $\sum_{i=1}^{n-1} r_i(\boldsymbol{x}) = -r_n(\boldsymbol{x})$ and

$$\begin{aligned}\boldsymbol{r}'(\boldsymbol{x}) \cdot \boldsymbol{w} &= \sum_{i=1}^{n-1} r_i(\boldsymbol{x}) \bigg(\frac{1}{M_i} \ln \frac{x_i}{x_{i\infty}} - \frac{1}{M_n} \ln \frac{x_n}{x_{n\infty}} \bigg) \\ &= \sum_{i=1}^{n-1} \frac{r_i(\boldsymbol{x})}{M_i} \ln \frac{x_i}{x_{i\infty}} - \frac{1}{M_n} \ln \frac{x_n}{x_{n\infty}} \sum_{i=1}^{n-1} r_i(\boldsymbol{x}) = \sum_{i=1}^{n} \frac{r_i(\boldsymbol{x})}{M_i} \ln \frac{x_i}{x_{i\infty}}. \end{aligned} \tag{18}$$

In view of definition (2) of r_i and $\boldsymbol{x}_\infty \in \mathcal{E}$, the last expression becomes

$$\begin{aligned}\boldsymbol{r}'(\boldsymbol{x}) \cdot \boldsymbol{w} &= \sum_{i=1}^{n} \sum_{a=1}^{N} (\beta_i^a - \alpha_i^a)(k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}) \ln \frac{x_i}{x_{i\infty}} \\ &= \sum_{i=1}^{n} \sum_{a=1}^{N} (k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}) \ln \frac{x_i^{\beta_i^a} x_{i\infty}^{\alpha_i^a}}{x_i^{\alpha_i^a} x_{i\infty}^{\beta_i^a}} \\ &= \sum_{a=1}^{N} (k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}) \ln \frac{\boldsymbol{x}^{\boldsymbol{\beta}^a} \boldsymbol{x}_\infty^{\boldsymbol{\alpha}^a}}{\boldsymbol{x}^{\boldsymbol{\alpha}^a} \boldsymbol{x}_\infty^{\boldsymbol{\beta}^a}} \end{aligned}$$

$$= \sum_{a=1}^{N} (k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}) \ln \frac{k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}}{k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a}} \leqslant 0,$$

because of the monotonicity of the logarithm. □

Taking into account Lemma 6, the estimations of Section 3.2 in [9] lead to the discrete entropy inequality

$$\begin{aligned} &\int_\Omega h((\boldsymbol{\rho}')^k)dz + C\tau \sum_{j=1}^k \sum_{i=1}^n \|\nabla (x_i^j)^{1/2}\|_{L^2(\Omega)}^2 + \tau \sum_{j=1}^k \sum_{i=1}^n \int_\Omega (-r_i(\boldsymbol{x}^j) \cdot \boldsymbol{w}^j) dz \\ &\quad + \varepsilon\tau \sum_{j=1}^k \sum_{i=1}^{n-1} \int_\Omega \bigg(\sum_{|\alpha|=l} (D^{\boldsymbol{\alpha}} w_i^j)^2 + (w_i^j)^2 \bigg) dz \leqslant \int_\Omega h((\boldsymbol{\rho}')^0_\eta) dz, \end{aligned} \tag{19}$$

where $(\boldsymbol{\rho}')^0_\eta$ is the vector of strictly positive approximations of the initial vector $(\boldsymbol{\rho}^0)' = (\rho_1^0, \ldots, \rho_{n-1}^0)^\top$ and $C > 0$ is a generic constant independent of τ and ε. This shows that

$$\tau \sum_{j=1}^k \|x_i^j\|_{H^1(\Omega)}^2 + \varepsilon\tau \sum_{j=1}^n \|w_i^j\|_{H^l(\Omega)}^2 \leqslant C, \quad i = 1, \ldots, n,$$

where $C > 0$ is independent of ε and τ. From these estimates and the boundedness of the reaction terms, we infer a uniform bound for the discrete time derivative,

$$\tau \sum_{k=1}^M \sum_{i=1}^{n-1} \big\|\tau^{-1}(\rho_i^k - \rho_i^{k-1})\big\|_{H^l(\Omega)'}^2 \leqslant C.$$

These estimates are sufficient to perform the limit $\varepsilon \to 0$ and $\tau \to 0$ in (17) as in Section 3.3 of [9] showing that the limit satisfies (15) and therefore is a global weak solution to (1)–(2).

Remark 7 (Discrete entropy inequality)**.** Before summing from $j = 1, \ldots, k$, we can formulate the discrete entropy inequality (19) as

$$E[\boldsymbol{x}^k|\boldsymbol{x}_\infty] + \tau D[\boldsymbol{x}^k] + C\varepsilon\tau \sum_{i=1}^{n-1} \|w_i^k\|_{H^l(\Omega)}^2 \leqslant E[\boldsymbol{x}^{k-1}|\boldsymbol{x}_\infty].$$

This estimate is the discrete analogue of (11) and it will be needed in the proof of part (iii) of Theorem 1; see Section 3.6. □

3. Convergence to equilibrium under detailed balance

In this section, we prove parts (ii) and (iii) of Theorem 1. First, we discuss the conservation laws and the existence of an equilibrium state.

3.1. **Conservation laws.** We set $R_i = r_i/M_i$, $\boldsymbol{J}_i = \boldsymbol{j}_i/M_i$ and $\boldsymbol{R} = (R_1, \dots, R_n)^\top$, $\mathbb{J} = (\boldsymbol{J}_1, \dots, \boldsymbol{J}_n)^\top$, $\boldsymbol{c} = (c_1, \dots, c_n)^\top$, where we recall that $c_i = \rho_i/M_i$. Dividing the ith-equation of (1) by M_i, we can reformulate them in vector form as

$$\partial_t \boldsymbol{c} + \operatorname{div} \mathbb{J} = \boldsymbol{R}. \tag{20}$$

Let $\mathbb{W} = (\beta_i^a - \alpha_i^a) \in \mathbb{R}^{n\times N}$ be the Wegscheider matrix and let $m = \dim\ker(\mathbb{W}^\top)$. Note that $m \geqslant 1$ since it follows from the conservation of total mass, $\sum_{i=1}^n r_i(\boldsymbol{x}) = 0$, that $\boldsymbol{M}^\top \mathbb{W} = 0$, i.e., the vector $\boldsymbol{M} = (M_1, \dots, M_n)^\top$ belongs to $\ker(\mathbb{W}^\top)$. Let the row vectors $\boldsymbol{q}_1, \dots, \boldsymbol{q}_m \in \mathbb{R}^{1\times n}$ be a basis of the left null space of $\mathbb{W}$, i.e. $\boldsymbol{q}_i \mathbb{W} = 0$ for $i = 1, \dots, m$. In particular, $\boldsymbol{q}_i^\top \in \ker(\mathbb{W}^\top)$. Finally, let $\mathbb{Q} = (Q_{ij}) \in \mathbb{R}^{m\times n}$ be the matrix with rows $\boldsymbol{q}_j$.

We claim that system (20) (with no-flux boundary conditions) possesses precisely m linear independent conservation laws.

Lemma 8 (Conservation laws)**.** *Let $\boldsymbol{\rho}$ be a weak solution to (1)-(2) in the sense of Theorem 3. Then the following conservation laws hold:*

$$\mathbb{Q}\overline{\boldsymbol{c}}(t) = \boldsymbol{M}^0, \quad t > 0,$$

where $\boldsymbol{M}^0 = \mathbb{Q}\overline{\boldsymbol{c}}^0$ is called the initial mass vector and $c_i^0 = \rho_i^0/M_i$, $i = 1, \dots, n$.

Note that, by changing the sign of the rows of $\mathbb{Q}$ if necessary, we can always choose $\mathbb{Q}$ such that $\boldsymbol{M}^0$ is positive componentwise.

Proof. We observe that the definitions of $\mathbb{Q}$ and $r_i(\boldsymbol{x}) = M_i R_i(\boldsymbol{x})$ in (2) imply that $\mathbb{Q}\boldsymbol{R} = 0$. Choosing $\boldsymbol{q}_j = (Q_{j1}, \dots,\ Q_{jn})$ as a test function in the weak formulation of (20) and observing that $\nabla \boldsymbol{q}_j = 0$, we find that

$$\int_0^t \int_\Omega \partial_t(\mathbb{Q}\boldsymbol{c})_j dz ds = \sum_{i=1}^n \int_0^t \int_\Omega \partial_t c_i Q_{ji} dz ds = \sum_{i=1}^n \int_0^t \int_\Omega R_i Q_{ji} dz ds = \int_0^t \int_\Omega (\mathbb{Q}\boldsymbol{R})_j dz ds = 0.$$

This shows that

$$\int_\Omega \mathbb{Q}\boldsymbol{c}(t) dz = \int_\Omega \mathbb{Q}\boldsymbol{c}^0 dz, \quad t > 0,$$

or $\mathbb{Q}\overline{\boldsymbol{c}}(t) = \mathbb{Q}\overline{\boldsymbol{c}}^0 =: \boldsymbol{M}^0$, where $c_i^0 = \rho_i^0/M_i$ is the initial concentration. □

Lemma 9. *There exists a row vector $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ such that $\boldsymbol{\zeta}\mathbb{Q} = \boldsymbol{M}^\top$ and $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$.*

Proof. Since $\boldsymbol{M}$ lies in the kernel of $\mathbb{W}^\top$ and the rows of $\mathbb{Q}$ form a basis of this space, we have $\boldsymbol{M} \in \ker(\mathbb{W}^\top) = \operatorname{ran}(\mathbb{Q}^\top)$. We infer that there exists a row vector $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ such that $\mathbb{Q}^\top \boldsymbol{\zeta}^\top = \boldsymbol{M}$ or $\boldsymbol{\zeta}\mathbb{Q} = \boldsymbol{M}^\top$. Moreover, by recalling $|\Omega| = 1$ and $\sum_{i=1}^n \rho_i^0 = 1$ in Ω,

$$1 = \int_\Omega \sum_{i=1}^n \rho_i^0 dz = \sum_{i=1}^n \overline{\rho_i}^0 = \sum_{i=1}^n M_i \overline{c_i}^0 = \boldsymbol{M}^\top \overline{\boldsymbol{c}}^0 = \boldsymbol{\zeta}\mathbb{Q}\overline{\boldsymbol{c}}^0 = \boldsymbol{\zeta}\boldsymbol{M}^0,$$

using the definition of $\boldsymbol{M}^0$ in Lemma 8. □

3.2. **Detailed-balanced condition.** The relative entropy (9) is formally a Lyapunov functional along the trajectories of (1)-(2) for $\boldsymbol{x}_\infty \in \mathcal{E}$. Note that $\mathcal{E}$ generally is a manifold of detailed-balanced equilibria. To identify uniquely the detailed-balanced equilibrium, we need to take into account the conservation laws. This subsection is concerned with the existence of a unique positive detailed-balanced equilibrium satisfying the conservation laws.

For chemical reaction networks in the context of ordinary differential equations (ODE), the existence of a unique equilibrium state was proved by Horn and Jackson [28]; also see [16]. The difficulty in this work lies in the fact that the reactions are modeled by molar fractions $\boldsymbol{x}$, while the conservation laws are presented by concentrations $\boldsymbol{c}$. Our idea is to enlarge the space $\mathbb{R}^n_+$ of concentrations $(c_1, \ldots, c_n)$ by adding the total concentration $c = \sum_{i=1}^n c_i \in \mathbb{R}_+$, which is considered to be an independent variable, and then to employ the ideas by Feinberg [16] to the augmented space $\mathbb{R}^{n+1}_+$. To this end, let

$$\boldsymbol{\omega} = (\omega_1, \ldots, \omega_{n+1}) = (c_1, \ldots, c_n, c), \tag{21}$$

and define the vectors in $\mathbb{R}^{n+1}$

$$\begin{aligned} \boldsymbol{\mu}^a &= \left(\alpha_1^a, \ldots, \alpha_n^a, \left(\sum_{i=1}^n (\beta_i^a - \alpha_i^a)\right)^+\right), \\ \boldsymbol{\nu}^a &= \left(\beta_1^a, \ldots, \beta_n^a, \left(\sum_{i=1}^n (\alpha_i^a - \beta_i^a)\right)^+\right), \end{aligned} \tag{22}$$

where $y^+ = \max\{0, y\}$. Finally, we write $\mathbf{1}_n = (1, \ldots, 1)^\top \in \mathbb{R}^n$ and $\mathbf{1}_{n+1} = (1, \ldots, 1)^\top \in \mathbb{R}^{n+1}$. The main result of this subsection is the following.

Theorem 10 (Existence of a unique detailed-balanced equilibrium)**.** *Assume that* (A2) *holds and let $\boldsymbol{M}^0 \in \mathbb{R}^m_+$ be an initial mass vector and $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ be a row vector such that $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. Then there exists a unique positive detailed-balanced equilibrium $\boldsymbol{x}_\infty \in \mathcal{E}$ satisfying the conservation laws and the normalization condition* (14)*.*

To prove Theorem 10 we first show the existence of an "equilibrium" in the augmented space.

Proposition 11. *Suppose the assumptions of Theorem 10 hold. Then there exists a unique $\boldsymbol{\omega} \in \mathbb{R}^{n+1}_+$ satisfying*

$$k_f^a \boldsymbol{\omega}^{\boldsymbol{\mu}^a} = k_b^a \boldsymbol{\omega}^{\boldsymbol{\nu}^a}, \quad a = 1, \ldots, N, \quad \widehat{\mathbb{Q}}\boldsymbol{\omega} = \widehat{\boldsymbol{M}}^0, \tag{23}$$

where $\widehat{\mathbb{Q}}$ and $\widehat{\boldsymbol{M}}^0$ are defined by

$$\widehat{\mathbb{Q}} = \begin{pmatrix} \mathbb{Q} & \mathbf{0} \\ \mathbf{1}_n^\top & -1 \end{pmatrix} \in \mathbb{R}^{(m+1)\times(n+1)}, \quad \widehat{\boldsymbol{M}}^0 = \begin{pmatrix} \boldsymbol{M}^0 \\ 0 \end{pmatrix} \in \mathbb{R}^{n+1}.$$

Before proving this result, we first show that Theorem 10 follows from Proposition 11.

Proof of Theorem 10. Let $\boldsymbol{\omega} = (c_{1\infty}, \ldots, c_{n\infty}, c_\infty)$ be the equilibrium in the augmented space constructed in Proposition 11. Define $x_{i\infty} = c_{i\infty}/c_\infty$. We will prove that $\boldsymbol{x}_\infty$ is an element of $\mathcal{E}$ and satisfies (14). Indeed, for any $a = 1, \ldots, N$, let $\gamma^a := \sum_{i=}^n (\alpha_i^a - \beta_i^a)$ and assume first that $\gamma^a \geqslant 0$. Then

$$k_f^a \prod_{i=1}^n c_{i\infty}^{\alpha_i^a} = k_f^a \boldsymbol{\omega}^{\boldsymbol{\mu}^a} = k_b^a \boldsymbol{\omega}^{\boldsymbol{\nu}^a} = k_b^a \prod_{i=1}^n c_{i\infty}^{\beta_i^a} c_\infty^{\gamma^a}$$

is equivalent to

$$k_f^a \boldsymbol{x}_\infty^{\boldsymbol{\alpha}^a} = k_f^a \prod_{i=1}^n c_{i\infty}^{\alpha_i^a} c_\infty^{-\sum_{i=1}^n \alpha_i^a} = k_b^a \prod_{i=1}^n c_{i\infty}^{\beta_i^a} c_\infty^{-\sum_{i=1}^n \beta_i^a} = k_b^a \boldsymbol{x}_\infty^{\boldsymbol{\beta}^a}.$$

The case $\gamma^a \leqslant 0$ can be treated in an analogous way. Thus, $\boldsymbol{x}_\infty \in \mathcal{E}$. It follows immediately from $\widehat{\mathbb{Q}}\boldsymbol{\omega} = \widehat{\boldsymbol{M}}^0$ that $\mathbb{Q}\boldsymbol{c}_\infty = \boldsymbol{M}^0$ and $\sum_{i=1}^n c_{i\infty} = c_\infty$. The latter identity implies that $\sum_{i=1}^n x_{i\infty} = 1$ due to $x_{i\infty} = c_{i\infty}/c_\infty$. Therefore $\boldsymbol{x}_\infty$ satisfies (14). ☐

The aim now is to prove Proposition 11. For this, we introduce the following definitions:

$$X_1 = \left\{ \boldsymbol{\omega} \in \mathbb{R}_+^{n+1} : \ k_f^a \boldsymbol{\omega}^{\boldsymbol{\mu}^a} = k_b^a \boldsymbol{\omega}^{\boldsymbol{\nu}^a} \text{ for } a = 1, \ldots, N \right\},$$

$$X_2 = \left\{ \boldsymbol{\omega} \in \mathbb{R}_+^{n+1} : \ \widehat{\mathbb{Q}}\boldsymbol{\omega} = \widehat{\boldsymbol{M}}^0 \right\}.$$

We argue that X_1 and X_2 are not empty. Indeed, due to (A2), there exists $\boldsymbol{x}_\infty \in \mathcal{E}$. Fix any $\omega_{n+1,\infty} \in (0, \infty)$ and define $\omega_{i\infty} = x_{i\infty}\omega_{n+1,\infty}$ for all $i = 1, \ldots, n$. We obtain immediately $\boldsymbol{\omega}_\infty = (\omega_{1\infty}, \ldots, \omega_{n+1,\infty}) \in X_1$. Concerning X_2, we see that there exists $\boldsymbol{\omega}' = (\omega_1, \ldots, \omega_n) \in \mathbb{R}_+^n$ such that $\mathbb{Q}\boldsymbol{\omega}' = \boldsymbol{M}^0$ since $\operatorname{rank}(\mathbb{Q}) = m < n$. By defining $\omega_{n+1} = \sum_{i=1}^n \omega_i$, we infer that $\boldsymbol{\omega} = (\boldsymbol{\omega}', \omega_{n+1}) \in X_2$.

Lemma 12. *Let $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ and $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ with $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$, let $\boldsymbol{\omega}_\infty \in X_1$ and $\boldsymbol{p} \in X_2$. Then the following statements are equivalent:*

- *There exists a unique vector $\boldsymbol{\omega} \in X_1 \cap X_2$.*
- *There exists a unique vector $\boldsymbol{\varphi}^* \in \operatorname{span}\{\boldsymbol{q}_1^\top, \ldots, \boldsymbol{q}_m^\top\}$ ($\boldsymbol{q}_i$ is the ith row of $\mathbb{Q}$) and a unique number $z_{m+1} \in \mathbb{R}$ such that*

$$\boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*} - e^{-z_{m+1}}\boldsymbol{p}' \in \ker \mathbb{Q}, \quad \langle e^{\boldsymbol{\varphi}^*}\boldsymbol{\omega}'_\infty, \mathbf{1}_n \rangle = \omega_{n+1,\infty}. \tag{24}$$

Here, we denote $\boldsymbol{p}' = (p_1, \ldots, p_n)$ and $\boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*}$ equals the vector with components $\omega_{i\infty}e^{\varphi_i^*}$, $i = 1, \ldots, n$. Observe that $\operatorname{span}\{\boldsymbol{q}_1^\top, \ldots, \boldsymbol{q}_m^\top\} = \operatorname{ran}(\mathbb{Q}^\top)$.

Proof. We first claim that

$$X_1 = \left\{ \boldsymbol{\omega} \in \mathbb{R}_+^{n+1} : \ \exists z_{m+1} \in \mathbb{R}, \ \boldsymbol{\varphi}^* \in \operatorname{ran}(\mathbb{Q}^\top) \text{ such that } \boldsymbol{\omega} = e^{z_{m+1}} \begin{pmatrix} \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*} \\ \omega_{n+1,\infty} \end{pmatrix} \right\}.$$

Indeed, $\boldsymbol{\omega} \in X_1$ holds if and only if $\boldsymbol{\omega}_\infty^{\boldsymbol{\nu}^a - \boldsymbol{\mu}^a} = k_f^a/k_b^a = \boldsymbol{\omega}^{\boldsymbol{\nu}^a - \boldsymbol{\mu}^a}$. Taking the logarithm componentwise, this becomes

$$\langle \log \boldsymbol{\omega}_\infty, \boldsymbol{\nu}^a - \boldsymbol{\mu}^a \rangle = \langle \log \boldsymbol{\omega}, \boldsymbol{\nu}^a - \boldsymbol{\mu}^a \rangle, \quad a = 1, \ldots, N.$$

This means that $\boldsymbol{\varphi} := \log(\boldsymbol{\omega}/\boldsymbol{\omega}_\infty) = \log \boldsymbol{\omega} - \log \boldsymbol{\omega}_\infty \in \ker\{\boldsymbol{\nu}^a - \boldsymbol{\mu}^a\}_{a=1,\ldots,N}$. By definition of $\boldsymbol{\mu}^a$ and $\boldsymbol{\nu}^a$, we know that

$$\ker\{\boldsymbol{\nu}^a - \boldsymbol{\mu}^a\}_{a=1,\ldots,N} = \operatorname{span}\big\{(\boldsymbol{q}_1^\top, 0)^\top, \ldots, (\boldsymbol{q}_m^\top, 0)^\top, \mathbf{1}_{n+1}\big\}.$$

Thus, there exist numbers $z_1, \ldots, z_{m+1} \in \mathbb{R}$ such that

$$\boldsymbol{\varphi} = \sum_{i=1}^m z_i \begin{pmatrix} \boldsymbol{q}_i^\top \\ 0 \end{pmatrix} + z_{m+1}\mathbf{1}_{n+1} = \begin{pmatrix} \boldsymbol{\varphi}^* + z_{m+1}\mathbf{1}_n \\ z_{m+1} \end{pmatrix},$$

where $\boldsymbol{\varphi}^* = \sum_{i=1}^m z_i \boldsymbol{q}_i^\top \in \operatorname{ran}(\mathbb{Q}^\top)$. It follows from the definition of $\boldsymbol{\varphi}$ that

$$\frac{\boldsymbol{\omega}}{\boldsymbol{\omega}_\infty} = e^{\boldsymbol{\varphi}} = \exp\begin{pmatrix} \boldsymbol{\varphi}^* + z_{m+1}\mathbf{1}_n \\ z_{m+1} \end{pmatrix} = e^{z_{m+1}} \begin{pmatrix} e^{\boldsymbol{\varphi}^*} \\ 1 \end{pmatrix}.$$

We conclude that $\boldsymbol{\omega} \in X_1$ if and only if

$$\boldsymbol{\omega} = \boldsymbol{\omega}_\infty e^{z_{m+1}} \begin{pmatrix} e^{\boldsymbol{\varphi}^*} \\ 1 \end{pmatrix} = e^{z_{m+1}} \begin{pmatrix} \boldsymbol{\omega}_\infty' e^{\boldsymbol{\varphi}^*} \\ \omega_{n+1,\infty} \end{pmatrix},$$

and this proves the claim.

Next, fixing $\boldsymbol{p} \in X_2$, it holds that $\boldsymbol{\omega} \in X_2$ if and only if

$$\begin{aligned} \mathbf{0} = \widehat{\mathbb{Q}}(\boldsymbol{\omega} - \boldsymbol{p}) &= \begin{pmatrix} \mathbb{Q} & \mathbf{0} \\ \mathbf{1}_n^\top & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega}' - \boldsymbol{p}' \\ \omega_{n+1} - p_{n+1} \end{pmatrix} \\ &= \begin{pmatrix} \mathbb{Q}(\boldsymbol{\omega}' - \boldsymbol{p}') \\ \langle \mathbf{1}_n, \boldsymbol{\omega}' - \boldsymbol{p}' \rangle - (\omega_{n+1} - p_{n+1}) \end{pmatrix}. \end{aligned}$$

Consequently, in view of the preceding claim, we have $\boldsymbol{\omega} \in X_1 \cap X_2$ if and only if

$$\mathbf{0} = \widehat{\mathbb{Q}}(\boldsymbol{\omega} - \boldsymbol{p}) = \begin{pmatrix} \mathbb{Q}(e^{z_{m+1}}\boldsymbol{\omega}_\infty' e^{\boldsymbol{\varphi}^*} - \boldsymbol{p}') \\ \langle \mathbf{1}_n, e^{z_{m+1}}\boldsymbol{\omega}_\infty' e^{\boldsymbol{\varphi}^*} - \boldsymbol{p}' \rangle - (e^{z_{m+1}}\omega_{n+1,\infty} - p_{n+1}) \end{pmatrix}.$$

The first n rows mean that $\boldsymbol{\omega}_\infty' e^{\boldsymbol{\varphi}*} - e^{-z_{m+1}}\boldsymbol{p}' \in \ker \mathbb{Q}$. Since $\boldsymbol{p} \in X_2$ and consequently $p_{n+1} = \sum_{i=1}^n p_i = \langle \mathbf{1}_n, \boldsymbol{p}' \rangle$, the last row simplifies to

$$0 = e^{z_{m+1}}\big(\langle e^{\boldsymbol{\varphi}^*}\boldsymbol{\omega}_\infty', \mathbf{1}_n \rangle - \omega_{n+1,\infty}\big).$$

This shows (24) and ends the proof. □

We need one more lemma.

Lemma 13. [16, Proposition B.1] *Let U be a linear subspace of $\mathbb{R}^n$ and $a = (a_1, \ldots, a_n), b = (b_1, \ldots, b_n) \in \mathbb{R}_+^n$. There exists a unique element $\mu = (\mu_1, \ldots, \mu_n) \in U^\perp$ such that*

$$ae^\mu - b \in U,$$

where $ae^\mu = (a_1 e^{\mu_1}, \ldots, a_n e^{\mu_n})$.

Proof of Proposition 11. Step 1: Existence. First, fixing $\boldsymbol{\omega}_\infty \in X_1$ and $\boldsymbol{p} \in X_2$, we claim that there exist $z_{m+1} \in \mathbb{R}$ and $\boldsymbol{\varphi}^* \in \operatorname{ran}(\mathbb{Q}^\top)$ such that (24) holds. We apply Lemma 13 with $U = \ker \mathbb{Q}$, $a = \boldsymbol{\omega}'_\infty$, and $b = e^{-z_{m+1}}\boldsymbol{p}'$, yielding the existence of a unique vector $\boldsymbol{\varphi}^*(z_{m+1}) \in U^\perp = \operatorname{ran}(\mathbb{Q}^\top)$ such that

$$\boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})} - e^{-z_{m+1}}\boldsymbol{p}' \in \ker \mathbb{Q}. \tag{25}$$

It remains to show the second equation in (24), i.e. to show that there exists a number $z^*_{m+1} \in \mathbb{R}$ such that $\langle e^{\boldsymbol{\varphi}^*(z^*_{m+1})}\boldsymbol{\omega}'_\infty, \mathbf{1}_n\rangle = \omega_{n+1,\infty}$. Then we set $\boldsymbol{\varphi}^* := \boldsymbol{\varphi}^*(z^*_{m+1})$, and (25) yields the first equation in (24).

We know that $\boldsymbol{M} \in \operatorname{span}\{\boldsymbol{q}_1^\top, \ldots, \boldsymbol{q}_m^\top\}$. Then (25) implies that

$$\left\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})} - e^{-z_{m+1}}\boldsymbol{p}', \boldsymbol{M}\right\rangle = 0 \quad \text{or} \quad \left\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \boldsymbol{M}\right\rangle = e^{-z_{m+1}}\langle \boldsymbol{p}', \boldsymbol{M}\rangle > 0.$$

We deduce that

$$\lim_{z_{m+1}\to+\infty}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \boldsymbol{M}\rangle = 0, \qquad \lim_{z_{m+1}\to-\infty}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \boldsymbol{M}\rangle = \infty.$$

Moreover, since

$$\frac{1}{M_{\max}}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \boldsymbol{M}\rangle \leqslant \langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \mathbf{1}_n\rangle \leqslant \frac{1}{M_{\min}}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \boldsymbol{M}\rangle,$$

it holds that

$$\lim_{z_{m+1}\to+\infty}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \mathbf{1}_n\rangle = 0, \qquad \lim_{z_{m+1}\to-\infty}\langle \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}^*(z_{m+1})}, \mathbf{1}_n\rangle = \infty.$$

By continuity, there exists $z^*_{m+1} \in \mathbb{R}$ such that $\langle e^{\boldsymbol{\varphi}^*(z^*_{m+1})}\boldsymbol{\omega}'_\infty, \mathbf{1}_n\rangle = \omega_{n+1,\infty}$.

Step 2: Uniqueness. Assume that there exist $(\widehat{\boldsymbol{\varphi}}, \widehat{z})$ and $(\breve{\boldsymbol{\varphi}}, \breve{z})$ with $\widehat{\boldsymbol{\varphi}}, \breve{\boldsymbol{\varphi}} \in \operatorname{ran}(\mathbb{Q}^\top)$ and $\widehat{z}, \breve{z} \in \mathbb{R}$ such that

$$\boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}} - e^{-\widehat{z}}\boldsymbol{p}',\ \boldsymbol{\omega}'_\infty e^{\breve{\boldsymbol{\varphi}}} - e^{-\breve{z}}\boldsymbol{p}' \in \ker \mathbb{Q}, \tag{26}$$

$$\langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \mathbf{1}_n\rangle = \omega_{n+1,\infty} = \langle \boldsymbol{\omega}'_\infty e^{\breve{\boldsymbol{\varphi}}}, \mathbf{1}_n\rangle. \tag{27}$$

From (26) it follows that

$$e^{\widehat{z}}\boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}} - e^{\breve{z}}\boldsymbol{\omega}'_\infty e^{\breve{\boldsymbol{\varphi}}} \in \ker \mathbb{Q}.$$

We infer from $\widehat{\boldsymbol{\varphi}} - \breve{\boldsymbol{\varphi}} \in \operatorname{ran}(\mathbb{Q}^\top) = \operatorname{span}\{\boldsymbol{q}_1^\top, \ldots, \boldsymbol{q}_m^\top\}$ that

$$\begin{aligned} 0 &= \left\langle e^{\widehat{z}}\boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}} - e^{\breve{z}}\boldsymbol{\omega}'_\infty e^{\breve{\boldsymbol{\varphi}}}, \widehat{\boldsymbol{\varphi}} - \breve{\boldsymbol{\varphi}}\right\rangle \\ &= e^{\breve{z}}\left\langle \boldsymbol{\omega}'_\infty (e^{\widehat{\boldsymbol{\varphi}}} - e^{\breve{\boldsymbol{\varphi}}}), (\widehat{\boldsymbol{\varphi}} - \breve{\boldsymbol{\varphi}})\right\rangle + (e^{\widehat{z}} - e^{\breve{z}})\left\langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \widehat{\boldsymbol{\varphi}} - \breve{\boldsymbol{\varphi}}\right\rangle =: I_1 + I_2. \end{aligned}$$

Hence, we have $I_2 = -I_1$ and because of

$$I_1 = e^{\breve{z}}\sum_{i=1}^n \omega_{i\infty}\big(e^{\widehat{\varphi}_i} - e^{\breve{\varphi}_i}\big)(\widehat{\varphi}_i - \breve{\varphi}_i) \geqslant 0,$$

it holds that $I_2 = -I_1 \leqslant 0$.

Now, if $\widehat{z} = \check{z}$, Lemma 13 shows that $\widehat{\boldsymbol{\varphi}} = \check{\boldsymbol{\varphi}}$, and the proof is finished. Thus, let us assume, without loss of generality, that $\widehat{z} > \check{z}$. Then the definition and nonpositivity of I_2 imply that

$$\langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \widehat{\boldsymbol{\varphi}} - \check{\boldsymbol{\varphi}} \rangle \leqslant 0. \tag{28}$$

Consider the function $f : \mathbb{R}^n \to \mathbb{R}$, $f(\boldsymbol{\varphi}) = \sum_{i=1}^n \omega_{i\infty} e^{\varphi_i}$. Then $\mathrm{D}f(\boldsymbol{\varphi}) = \boldsymbol{\omega}'_\infty e^{\boldsymbol{\varphi}}$ and $\mathrm{D}^2 f(\boldsymbol{\varphi}) = \operatorname{diag}(\omega_{i\infty} e^{\varphi_i})_{i=1,\ldots,n}$ and so, f is strictly convex. Hence, by (27),

$$\begin{aligned} \langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \widehat{\boldsymbol{\varphi}} - \check{\boldsymbol{\varphi}} \rangle &= \langle \mathrm{D}f(\widehat{\boldsymbol{\varphi}}), \widehat{\boldsymbol{\varphi}} - \check{\boldsymbol{\varphi}} \rangle \geqslant f(\widehat{\boldsymbol{\varphi}}) - f(\check{\boldsymbol{\varphi}}) \\ &= \langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \mathbf{1}_n \rangle - \langle \boldsymbol{\omega}'_\infty e^{\check{\boldsymbol{\varphi}}}, \mathbf{1}_n \rangle = 0. \end{aligned}$$

We deduce from this identity and (28) that $\langle \boldsymbol{\omega}'_\infty e^{\widehat{\boldsymbol{\varphi}}}, \widehat{\boldsymbol{\varphi}} - \check{\boldsymbol{\varphi}} \rangle = 0$ and consequently, $I_2 = 0$ and $I_1 = -I_2 = 0$. By the monotonicity of the exponential function, we infer that $\widehat{\boldsymbol{\varphi}} = \check{\boldsymbol{\varphi}}$. Then, taking the difference of the two vectors in (26), we have $(e^{-\widehat{z}} - e^{-\check{z}})\boldsymbol{p}' \in \ker \mathbb{Q}$. Since $\widehat{z} \neq \check{z}$, this shows that $\boldsymbol{p}' \in \ker \mathbb{Q}$ and therefore $\mathbb{Q}\boldsymbol{p}' = \mathbf{0}$ contradicting the fact that $\boldsymbol{p} \in X_2$ and in particular $\mathbb{Q}\boldsymbol{p}' = \boldsymbol{M}^0 \neq \mathbf{0}$. Thus, $\widehat{z}$ and $\check{z}$ must coincide, and uniqueness holds. ☐

Remark 14 (Boundary equilibria and Global Attractor Conjecture)**.** Besides the unique positive detailed-balanced equilibrium obtained in Theorem 10, there might exist (possibly infinitely many) boundary equilibria $\boldsymbol{x}^* \in \partial\mathcal{E}$. The convergence of solutions to reaction systems towards the positive equilibrium under the presence of boundary equilibria is a subtle problem, even in the ODE setting. The main reason is that if a trajectory converges to a boundary equilibrium, the entropy production $D[\boldsymbol{x}]$ vanishes while the relative entropy $E[\boldsymbol{x}|\boldsymbol{x}_\infty]$ remains positive, which means that the entropy-production inequality (13) is not true in general. However, it is conjectured, still in the ODE setting, that the positive detailed-balanced equilibrium is the only attracting point despite the presence of boundary equilibria. This is called the *Global Attractor Conjecture*, and it is considered as one of the most important problems in chemical reaction network theory; see, e.g., [1, 23] for partial answers. Recently, a full proof of this conjecture in the ODE setting has been proposed in [11], but the result is still under verification. See also [13, 20] for reaction-diffusion systems possessing boundary equilibria. ☐

3.3. **Preliminary estimates for the entropy and entropy production.** We derive some estimates for the relative entropy (9) and the entropy production (12) from below and above. In the following, let $\rho_1, \ldots, \rho_n : \Omega \to [0, \infty)$ be integrable functions such that $\sum_{i=1}^n \rho_i = 1$ in Ω and set $c_i = \rho_i/M_i$ and $x_i = c_i/c$ for $i = 1, \ldots, n$. We assume that the functions have the same regularity as the weak solutions from Theorem 3. For later reference, we note the following inequalities, which give bounds on the total concentration only depending on the molar masses:

$$\frac{1}{M_{\max}} \leqslant c = \sum_{i=1}^n \frac{\rho_i}{M_i} \leqslant \frac{1}{M_{\min}} \quad \text{in } \Omega, \tag{29}$$

where $M_{\max} = \max_{i=1,\ldots,n} M_i$ and $M_{\min} = \min_{i=1,\ldots,n} M_i$. Moreover, given the unique equilibrium $\boldsymbol{x}_\infty$ according to Theorem 10, we observe that $\sum_{i=1}^n \rho_{i\infty}/M_i = \sum_{i=1}^n c_{i\infty} =$

$c_\infty \sum_{i=1}^n x_{i\infty} = c_\infty$, and consequently,

$$\frac{1}{M_{\max}} \leqslant c_\infty \leqslant \frac{1}{M_{\min}}. \tag{30}$$

Lemma 15. *There exists a constant $C > 0$, only depending on $M_{\min}$, $M_{\max}$, and $\boldsymbol{x}_\infty$, such that*

$$E[\boldsymbol{x}|\boldsymbol{x}_\infty] \leqslant C \sum_{i=1}^n \bigg(\int_\Omega \Big(c_i^{1/2} - \overline{c_i^{1/2}}\Big)^2 dz + \big(\overline{c_i}^{1/2} - c_{i\infty}^{1/2}\big)^2 \bigg).$$

Proof. We use $\sum_{i=1}^n x_i = \sum_{i=1}^n x_{i\infty} = 1$ to reformulate the relative entropy

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &= \sum_{i=1}^n \int_\Omega c\bigg(x_i \ln \frac{x_i}{x_{i\infty}} - x_i + x_{i\infty} \bigg) dz \\ &= \sum_{i=1}^n \int_\Omega c x_{i\infty} \bigg(\frac{x_i}{x_{i\infty}} \ln \frac{x_i}{x_{i\infty}} - \frac{x_i}{x_{i\infty}} + 1 \bigg) dz. \end{aligned}$$

The function $\Phi(y) = (y \ln y - y + 1)/(y^{1/2} - 1)^2$ is continuous and nondecreasing on $\mathbb{R}_+$. Therefore, using (29),

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &= \sum_{i=1}^n \int_\Omega c x_{i\infty} \Phi\bigg(\frac{x_i}{x_{i\infty}} \bigg) \bigg(\bigg(\frac{x_i}{x_{i\infty}} \bigg)^{1/2} - 1 \bigg)^2 dz \\ &\leqslant \frac{1}{M_{\min}} \sum_{i=1}^n \Phi\bigg(\frac{1}{x_{i\infty}} \bigg) \frac{1}{x_{i\infty}} \int_\Omega (x_i - x_{i\infty})^2 dz \leqslant C \sum_{i=1}^n \int_\Omega (x_i - x_{i\infty})^2 dz \end{aligned} \tag{31}$$

for some constant $C > 0$ only depending on $M_{\min}$ and $\boldsymbol{x}_\infty$.

It remains to formulate the square on the right-hand side in terms of the partial concentrations. To this end, we set $f_i(\boldsymbol{c}) = c_i/c$ for $\boldsymbol{c} = (c_1, \ldots, c_n)$ and $c = \sum_{j=1}^n c_j$. By definition of the molar fractions x_i and $x_{i\infty}$, we have $x_i = f_i(\boldsymbol{c})$ and $x_{i\infty} = f_i(\boldsymbol{c}_\infty)$. The estimates

$$\bigg| \frac{\partial f_i}{\partial c_j}(\boldsymbol{c}) \bigg| \leqslant \frac{1}{c} \leqslant M_{\max}, \quad \bigg| \frac{\partial f_i}{\partial c_j}(\boldsymbol{c}_\infty) \bigg| \leqslant \frac{1}{c_\infty} \leqslant M_{\max}$$

imply that, for some $\boldsymbol{\xi}$ on the line between $\boldsymbol{c}$ and $\boldsymbol{c}_\infty$,

$$\begin{aligned} \int_\Omega (x_i - x_{i\infty})^2 dz &= \int_\Omega (f_i(\boldsymbol{c}) - f_i(\boldsymbol{c}_\infty))^2 dz = \sum_{j=1}^n \int_\Omega \bigg(\frac{\partial f_i}{\partial c_j}(\boldsymbol{\xi}) \bigg)^2 (c_j - c_{j\infty})^2 dz \\ &\leqslant M_{\max}^2 \sum_{j=1}^n \int_\Omega \big(c_j^{1/2} + c_{j\infty}^{1/2}\big)^2 \big(c_j^{1/2} - c_{j\infty}^{1/2}\big)^2 dz \\ &\leqslant M_{\max}^2 \bigg(\frac{2}{M_{\min}^{1/2}} \bigg)^2 \sum_{i=1}^n \int_\Omega \big(c_i^{1/2} - c_{i\infty}^{1/2}\big)^2 dz \\ &\leqslant C \sum_{i=1}^n \int_\Omega \big(c_i^{1/2} - c_{i\infty}^{1/2}\big)^2 dz, \end{aligned}$$

and $C>0$ depends only on $M_{\min}$, $M_{\max}$, and $\boldsymbol{x}_\infty$. Combining this estimate with (31) leads to (here, we use that $|\Omega|=1$)

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &\leqslant C\sum_{i=1}^n\int_\Omega\big(c_i^{1/2}-c_{i\infty}^{1/2}\big)^2dz \\ &\leqslant 2C\sum_{i=1}^n\bigg(\int_\Omega\Big(c_i^{1/2}-\overline{c_i^{1/2}}\Big)^2dz+\Big(\overline{c_i^{1/2}}-c_{i\infty}^{1/2}\Big)^2\bigg) \\ &\leqslant 2C\sum_{i=1}^n\bigg(\int_\Omega\Big(c_i^{1/2}-\overline{c_i^{1/2}}\Big)^2dz+2\Big(\overline{c_i^{1/2}}-\overline{c_i}^{1/2}\Big)^2+2\big(\overline{c_i}^{1/2}-c_{i\infty}^{1/2}\big)^2\bigg). \end{aligned} \tag{32}$$

We wish to estimate the second term. The Cauchy–Schwarz inequality gives $\overline{c_i^{1/2}}\leqslant\overline{c_i}^{1/2}$ and hence

$$\begin{aligned} \Big(\overline{c_i^{1/2}}-\overline{c_i}^{1/2}\Big)^2 &= \Big(\overline{c_i^{1/2}}\Big)^2+\overline{c_i}-2\overline{c_i^{1/2}}\,\overline{c_i}^{1/2} \\ &\leqslant \Big(\overline{c_i^{1/2}}\Big)^2+\overline{c_i}-2\overline{c_i^{1/2}}\,\overline{c_i^{1/2}}=\int_\Omega\Big(c_i^{1/2}-\overline{c_i^{1/2}}\Big)^2dz. \end{aligned}$$

Putting this into (32), it follows that

$$E[\boldsymbol{x}|\boldsymbol{x}_\infty]\leqslant 2C\sum_{i=1}^n\bigg(3\int_\Omega\Big(c_i^{1/2}-\overline{c_i^{1/2}}\Big)^2dz+2\big(\overline{c_i}^{1/2}-c_{i\infty}^{1/2}\big)^2\bigg),$$

and we conclude the proof. □

Lemma 16. *There exists a constant $C>0$, only depending on $M_{\min}$ and $M_{\max}$, such that*

$$D[\boldsymbol{x}]\geqslant C\left[\sum_{i=1}^n\int_\Omega|\nabla c_i^{1/2}|^2dz+\int_\Omega|\nabla c^{1/2}|^2dz+\sum_{a=1}^N\int_\Omega\big(k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a}\big)\ln\frac{k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a}}dz\right].$$

Proof. Lemma 5 shows that the first term in $D[\boldsymbol{x}]$ can be estimated from below:

$$\int_\Omega\nabla\boldsymbol{w}:\mathbb{B}(\boldsymbol{w})\nabla\boldsymbol{w}dz\geqslant C_B\sum_{i=1}^n\int_\Omega|\nabla x_i^{1/2}|^2dz.$$

We claim that we can relate $\sum_{i=1}^n|\nabla x_i^{1/2}|^2$ and $|\nabla c^{1/2}|^2$. For this, we proceed as in [9, page 494]. We infer from the definition $x_i=c_i/c$ that $c\sum_{i=1}^nM_ix_i=\sum_{i=1}^nM_ic_i=\sum_{i=1}^n\rho_i=1$. Therefore, inserting $c=1/\sum_{i=1}^nM_ix_i$ and using the Cauchy–Schwarz inequality,

$$\begin{aligned} |\nabla c^{1/2}|^2 &= \frac{1}{4c}|\nabla c|^2=\frac{1}{4c}\left|\frac{-\sum_{i=1}^nM_i\nabla x_i}{(\sum_{i=1}^nM_ix_i)^2}\right|^2=c^3\left|\sum_{i=1}^nM_ix_i^{1/2}\nabla x_i^{1/2}\right|^2 \\ &\leqslant nc^3\sum_{i=1}^nM_i^2x_i|\nabla x_i^{1/2}|^2\leqslant\frac{nM_{\max}^2}{M_{\min}^3}\sum_{i=1}^n|\nabla x_i^{1/2}|^2, \end{aligned} \tag{33}$$

where we used $c \leqslant 1/M_{\min}$ (see (29)). Similarly, employing (33),

$$\begin{aligned}\sum_{i=1}^n |\nabla c_i^{1/2}|^2 &= \sum_{i=1}^n |\nabla (cx_i)^{1/2}|^2 \leqslant 2\sum_{i=1}^n x_i|\nabla c^{1/2}|^2 + 2\sum_{i=1}^n c|\nabla x_i^{1/2}|^2 \\ &= 2|\nabla c^{1/2}|^2 + 2c\sum_{i=1}^n |\nabla x_i^{1/2}|^2 \leqslant C\sum_{i=1}^n |\nabla x_i^{1/2}|^2, \end{aligned} \tag{34}$$

where $C > 0$ depends only on $M_{\min}$ and $M_{\max}$. Adding (33) and (34) and integrating over Ω then shows that, for another constant $C > 0$,

$$\sum_{i=1}^n \int_\Omega |\nabla x_i^{1/2}|^2 \geqslant C\bigg(\sum_{i=1}^n \int_\Omega |\nabla c_i^{1/2}|^2 dz + \int_\Omega |\nabla c^{1/2}|^2 dz\bigg).$$

The lemma then follows from definition (12) of $D[\boldsymbol{x}]$. □

Lemma 17. *There exists a constant $C_{\rm CKP} > 0$, only depending on $M_{\max}$, such that*

$$E[\boldsymbol{x}|\boldsymbol{x}_\infty] \geqslant C_{\rm CKP}\sum_{i=1}^n \|x_i - x_{i\infty}\|_{L^1(\Omega)}^2.$$

Proof. The estimate is a consequence of the Csiszár–Kullback–Pinsker inequality. Since we are interested in the constant, we provide the (short) proof. We recall that $1/M_{\max} \leqslant c \leqslant 1/M_{\min}$. Arguing as in (31) and using $\Phi(y) \geqslant 1$ for $y \in \mathbb{R}_+$, we obtain

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &= \sum_{i=1}^n \int_\Omega cx_{i\infty}\bigg(\frac{x_i}{x_{i\infty}}\ln\frac{x_i}{x_{i\infty}} - \frac{x_i}{x_{i\infty}} + 1\bigg)dz \\ &= \sum_{i=1}^n \int_\Omega cx_{i\infty}\Phi\bigg(\frac{x_i}{x_{i\infty}}\bigg)\bigg(\bigg(\frac{x_i}{x_{i\infty}}\bigg)^{1/2} - 1\bigg)^2 dz \\ &\geqslant \frac{1}{M_{\max}}\sum_{i=1}^n \int_\Omega (x_i^{1/2} - x_{i\infty}^{1/2})^2 dz. \end{aligned}$$

Then, by the Cauchy–Schwarz inequality and the bounds $x_i \leqslant 1$, $x_{i\infty} \leqslant 1$,

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &\geqslant \frac{1}{M_{\max}}\sum_{i=1}^n \bigg(\int_\Omega |x_i^{1/2} - x_{i\infty}^{1/2}|dz\bigg)^2 \\ &= \frac{1}{M_{\max}}\sum_{i=1}^n \bigg(\int_\Omega \frac{|x_i - x_{i\infty}|}{x_i^{1/2} + x_{i\infty}^{1/2}}dz\bigg)^2 \\ &\geqslant \frac{1}{4M_{\max}}\sum_{i=1}^n \bigg(\int_\Omega |x_i - x_{i\infty}|dz\bigg)^2. \end{aligned}$$

This finishes the proof. □

3.4. **The case of equal homogeneities.** The aim of this and the following subsection is the proof of the functional inequality $D[\boldsymbol{x}] \geqslant \lambda E[\boldsymbol{x}|\boldsymbol{x}_\infty]$ for some $\lambda > 0$. For this, we will distinguish two cases, the case which we call *equal homogeneities*,

$$\sum_{i=1}^n \alpha_i^a = \sum_{i=1}^n \beta_i^a \quad \text{for all } a = 1, \ldots, N, \tag{35}$$

and the case of *unequal homogeneities*: There exists $a \in \{1, \ldots, N\}$ such that

$$\sum_{i=1}^n \alpha_i^a \neq \sum_{i=1}^n \beta_i^a. \tag{36}$$

This subsection is concerned with the first case.

Proposition 18 (Entropy entropy-production inequality; case of equal homogeneities)**.** *Fix $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ such that $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. Let $\boldsymbol{x}_\infty$ be the equilibrium constructed in Theorem 10. Assume that (35) holds and system (1)–(2) has no boundary equilibria. Then there exists a constant $\lambda > 0$, which is constructive up to a finite-dimensional inequality, such that*

$$D[\boldsymbol{x}] \geqslant \lambda E[\boldsymbol{x}|\boldsymbol{x}_\infty]$$

for all functions $\boldsymbol{x} : \Omega \to \mathbb{R}_+^n$ having the same regularity as the corresponding solutions in Theorem 3, and satisfying $\mathbb{Q}\overline{\boldsymbol{c}} = \boldsymbol{M}^0$.

Proof. We use Lemma 15 and the Poincaré inequality to obtain

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &\leqslant C \sum_{i=1}^n \bigg(\int_\Omega \Big(c_i^{1/2} - \overline{c_i^{1/2}} \Big)^2 dz + \big(\overline{c_i}^{1/2} - c_{i\infty}^{1/2} \big)^2 \bigg) \\ &\leqslant C \sum_{i=1}^n \bigg\{ \int_\Omega |\nabla c_i^{1/2}|^2 dz + \bigg(\Big(\frac{\overline{c_i}}{c_{i\infty}} \Big)^{1/2} - 1 \bigg)^2 \bigg\}. \end{aligned}$$

Next, we take into account estimate [20, formula (11)] and [20, Lemma 2.7]:

$$\begin{aligned} E[\boldsymbol{x}|\boldsymbol{x}_\infty] &\leqslant C \sum_{i=1}^n \int_\Omega |\nabla c_i^{1/2}|^2 dz + \frac{C}{H_1} \sum_{a=1}^N \bigg\{ \bigg(\sqrt{\frac{\overline{\boldsymbol{c}}}{\boldsymbol{c}_\infty}} \bigg)^{\boldsymbol{\alpha^a}} - \bigg(\sqrt{\frac{\overline{\boldsymbol{c}}}{\boldsymbol{c}_\infty}} \bigg)^{\boldsymbol{\beta^a}} \bigg\}^2 \\ &\leqslant C \sum_{i=1}^n \int_\Omega |\nabla c_i^{1/2}|^2 dz + C \sum_{a=1}^N \big(k_f^a \boldsymbol{c}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{c}^{\boldsymbol{\beta}^a} \big) \ln \frac{k_f^a \boldsymbol{c}^{\boldsymbol{\alpha}^a}}{k_b^a \boldsymbol{c}^{\boldsymbol{\beta}^a}}, \end{aligned} \tag{37}$$

where $H_1 > 0$ is the constant in the finite-dimensional inequality (11) of [20]. Observe that we can apply the results [20] since $\mathbb{Q}\overline{\boldsymbol{c}} = \boldsymbol{M}^0$ is satisfied; see Lemma 8.

We claim that the last term is smaller or equal $D[\boldsymbol{x}]$. Indeed, inserting the expression $x_i = c_i/c$ in the last term of the entropy production (12) and employing assumption (35), it follows that

$$\sum_{a=1}^N \int_\Omega (k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}) \ln \frac{k_f^a \boldsymbol{x}^{\boldsymbol{\alpha}^a}}{k_b^a \boldsymbol{x}^{\boldsymbol{\beta}^a}} dz = \sum_{a=1}^N \int_\Omega \frac{1}{c^{\alpha_1^a + \cdots \alpha_n^a}} (k_f^a \boldsymbol{c}^{\boldsymbol{\alpha}^a} - k_b^a \boldsymbol{c}^{\boldsymbol{\beta}^a}) \ln \frac{k_f^a \boldsymbol{c}^{\boldsymbol{\alpha}^a}}{k_b^a \boldsymbol{c}^{\boldsymbol{\beta}^a}} dz$$

$$\geqslant C\sum_{a=1}^N\int_\Omega (k_f^a\boldsymbol{c}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{c}^{\boldsymbol{\beta}^a})\ln\frac{k_f^a\boldsymbol{c}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{c}^{\boldsymbol{\beta}^a}}dz, \tag{38}$$

where we used in the last step $M_{\min}\leqslant 1/c\leqslant M_{\max}$. By Lemma 16, this shows that

$$D[\boldsymbol{x}]\geqslant C\sum_{i=1}^n\int_\Omega|\nabla c_i^{1/2}|^2dz+C\sum_{a=1}^N\int_\Omega (k_f^a\boldsymbol{c}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{c}^{\boldsymbol{\beta}^a})\ln\frac{k_f^a\boldsymbol{c}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{c}^{\boldsymbol{\beta}^a}}dz,$$

and combining this estimate with (37) concludes the proof. □

3.5. **The case of unequal homogeneities.** In this subsection, we consider the case (36) of unequal homogeneities. Since we cannot replace $\boldsymbol{x}$ easily by $\boldsymbol{c}$ as in (38), the estimates are much more involved than in the case of equal homogeneities. Similar as in Section 3.2, our idea is to introduce c as a new variable and to lift the problem from the n variables $c_1,\ldots,c_n$ to the $n+1$ variables $c_1,\ldots,c_n,c$. Then $D[\boldsymbol{x}]$ is represented by $n+1$ variables $c_1,\ldots,c_n,c$ under the conservation laws $\mathbb{Q}\overline{\boldsymbol{c}}=\boldsymbol{M}^0$ and the additional constraint $c=\sum_{i=1}^n c_i$ and thus $\overline{c}=\sum_{i=1}^n\overline{c_i}$. We employ the notation (21) and (22).

First, let $\gamma^a:=\sum_{i=1}^n(\alpha_i^a-\beta_i^a)$ and assume that $\gamma^a\geqslant 0$. With the definitions $x_i=c_i/c$, $\omega_i=c_i$ for $i=1,\ldots,n$, and $\omega_{n+1}=c$, we compute

$$\begin{aligned}
&\sum_{a=1}^N\int_\Omega (k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a})\ln\frac{k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a}}dz\\
&\quad=\sum_{a=1}^N\int_\Omega\left\{k_f^a\prod_{i=1}^n\left(\frac{c_i}{c}\right)^{\alpha_i^a}-k_b^a\prod_{i=1}^n\left(\frac{c_i}{c}\right)^{\beta_i^a}\right\}\ln\frac{k_f^a\prod_{i=1}^n(c_i/c)^{\alpha_i^a}}{k_b^a\prod_{i=1}^n(c_i/c)^{\beta_i^a}}dz\\
&\quad=\sum_{a=1}^N\int_\Omega\frac{1}{c^{\sum_{i=1}^n\alpha_i^a}}\left(k_f^a\prod_{i=1}^n c_i^{\alpha_i^a}-k_b^ac^{\gamma^a}\prod_{i=1}^n c_i^{\beta_i}\right)\ln\frac{k_f^a\prod_{i=1}^n c_i^{\alpha_i^a}}{k_b^ac^{\gamma^a}\prod_{i=1}^n c_i^{\beta_i}}dz\\
&\quad=\sum_{a=1}^N\int_\Omega\frac{1}{c^{\sum_{i=1}^n\alpha_i^a}}\left(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}-k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\right)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz\\
&\quad\geqslant C\int_\Omega\left(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}-k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\right)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz,
\end{aligned}$$

where $C>0$ depends on $M_{\max}$. In the case $\gamma^a<0$, we argue in the same way, leading to

$$\begin{aligned}
\sum_{a=1}^N\int_\Omega (k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}-k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a})\ln\frac{k_f^a\boldsymbol{x}^{\boldsymbol{\alpha}^a}}{k_b^a\boldsymbol{x}^{\boldsymbol{\beta}^a}}dz&=\sum_{a=1}^N\int_\Omega\frac{1}{c^{\sum_{i=1}^n\beta_i^a}}\left(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}-k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\right)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz\\
&\geqslant C\int_\Omega\left(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}-k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\right)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz.
\end{aligned}$$

Consequently, taking into account Lemma 16, we find that

$$D[\boldsymbol{x}]\geqslant\widetilde{D}[\boldsymbol{\omega}]:=C\sum_{i=1}^{n+1}\int_\Omega|\nabla\omega_i^{1/2}|^2dz+C\sum_{a=1}^N\int_\Omega\left(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}-k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\right)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz. \tag{39}$$

We need to determine the conservation laws for $\overline{\boldsymbol{\omega}}$. We write $\mathbf{1} = (1, \ldots, 1)^\top \in \mathbb{R}^{n+1}$.

Lemma 19. *Assume that* $\mathbb{Q}\overline{\boldsymbol{c}} = \boldsymbol{M}^0$. *Then* $\overline{\boldsymbol{\omega}} = (\overline{c_1}, \ldots, \overline{c_n}, \overline{c})$ *satisfies the conservation laws*

$$\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0,$$

where $\widehat{\mathbb{Q}}$ *and* $\widehat{\boldsymbol{M}}^0$ *are defined by*

$$\widehat{\mathbb{Q}} = \begin{pmatrix} \mathbb{Q} & \mathbf{0} \\ \mathbf{1}^\top & -1 \end{pmatrix} \in \mathbb{R}^{(m+1)\times(n+1)}, \quad \widehat{\boldsymbol{M}}^0 = \begin{pmatrix} \boldsymbol{M}^0 \\ 0 \end{pmatrix} \in \mathbb{R}^{n+1}. \tag{40}$$

Proof. The result follows from a direct computation:

$$\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \begin{pmatrix} \mathbb{Q} & \mathbf{0} \\ \mathbf{1} & -1 \end{pmatrix} \begin{pmatrix} \overline{\omega_1} \\ \vdots \\ \overline{\omega_n} \\ \overline{\omega_{n+1}} \end{pmatrix} = \begin{pmatrix} \mathbb{Q}\overline{\boldsymbol{c}} \\ \sum_{i=1}^n \overline{c_i} - \overline{c} \end{pmatrix} = \begin{pmatrix} \boldsymbol{M}^0 \\ 0 \end{pmatrix},$$

since it holds that $\overline{c} = \sum_{i=1}^n \overline{c_i}$. □

Lemma 20. *There exists a constant* $C > 0$, *depending on* Ω, n, N, k_f^a, k_b^a $(a = 1, \ldots, N)$, *and* M_i $(i = 1, \ldots, n)$, *such that*

$$\widetilde{D}[\boldsymbol{\omega}] \geqslant C \sum_{a=1}^N \left((k_f^a)^{1/2} \sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a} \right)^2,$$

for all measurable functions $\boldsymbol{\omega} : \Omega \to \mathbb{R}_+^{n+1}$ *such that* $\widetilde{D}[\boldsymbol{\omega}]$ *is finite, with* $\widetilde{D}[\boldsymbol{\omega}]$ *defined in* (39).

A similar but slightly simpler result for reaction-diffusion systems is proved in [20, Lemma 2.7]. The proof of this lemma is lengthy and therefore shifted to Appendix A. We remark that the validity of this lemma applies to all measurable functions with $\widetilde{D}[\boldsymbol{\omega}] < +\infty$.

Lemma 21. *Assume that* (1)–(2) *possesses no boundary equilibria. Fix* $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ *such that* $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. *Then there exists a nonconstructive constant* $C > 0$ *such that for all* $\overline{\boldsymbol{\omega}} \in \mathbb{R}_+^{n+1}$ *satisfying* $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0$, *it holds that*

$$\sum_{a=1}^N \left((k_f^a)^{1/2} \sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a} \right)^2 \geqslant C \sum_{i=1}^{n+1} \left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2} \right)^2, \tag{41}$$

where $\boldsymbol{\omega}_\infty$ *is constructed in Proposition 11.*

Remark 22. We mark that this lemma is proved for *any* vector $\overline{\boldsymbol{\omega}} \in \mathbb{R}_+^{n+1}$ satisfying the conservation laws. It does not use any analytical properties of solutions to (1)-(2). The notation $\overline{\boldsymbol{\omega}}$ is a bit abusive, since we later apply this lemma to the average $\overline{\boldsymbol{\omega}}$, where $\boldsymbol{\omega}$ is constructed from solutions to (1)-(2).

Remark 23. While all the constants before and after this lemma are constructive, this is not the case for the constant in Lemma 21, since the lemma is proved by using a contradiction argument. Still, inequality (41) is finite-dimensional. Therefore, in the general case, the rate of convergence to equilibrium to system (1)-(2) is constructive up to the finite-dimensional inequality (41). We present in Section 4 an example for which (41) can be proved with a constructive (even explicit) constant, which consequently leads to a constructive rate of convergence to equilibrium for (1)-(2). $\square$

Proof of Lemma 21. We first show that $\overline{\boldsymbol{\omega}}$ is bounded. Indeed, we infer from $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0$ that $\mathbb{Q}\overline{\boldsymbol{\omega}}' = \boldsymbol{M}^0$. Thus, $1 = \boldsymbol{\zeta}\boldsymbol{M}^0 = \boldsymbol{\zeta}\mathbb{Q}\overline{\boldsymbol{\omega}} = \sum_{i=1}^n M_i\overline{\omega_i}$. Hence, $\overline{\omega_i} \leqslant 1/M_{\min}$ and consequently $\overline{\omega}_{n+1} = \sum_{i=1}^n \overline{\omega_i} \leqslant n/M_{\min}$.

We will now prove that

$$\lambda := \inf_{\overline{\boldsymbol{\omega}}\in\mathbb{R}_+^{n+1}:\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}}=\widehat{\boldsymbol{M}}^0} \frac{\sum_{a=1}^N \left((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\right)^2}{\sum_{i=1}^{n+1}\left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2}\right)^2} > 0.$$

It is obvious that $\lambda \geqslant 0$. Since the denominator is bounded from above, $\lambda = 0$ can occur only if the nominator approaches zero. In view of Proposition 11 and the fact that the system is assumed to have no boundary equilibria, the nominator can converge to zero only when $\overline{\boldsymbol{\omega}} \to \boldsymbol{\omega}_\infty$. Therefore, $\lambda = 0$ is only possible if $\delta = 0$, where δ is the linearized version of λ defined in Lemma 24 below. Setting $\eta_i = \overline{\omega_i} - \omega_{i\infty}$, Lemma 24 shows that $\delta = 0$ if and only if

$$0 = \liminf_{\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}}=\widehat{\boldsymbol{M}}^0,\,\overline{\boldsymbol{\omega}}\to\boldsymbol{\omega}_\infty} \frac{\sum_{a=1}^N k_f^a\boldsymbol{\omega}_\infty^{\boldsymbol{\mu}^a}\left\{\sum_{i=1}^{n+1}(\mu_i^a - \nu_i^a)\eta_i\omega_{i\infty}^{-1}\right\}^2}{\sum_{i=1}^{n+1}\eta_i^2\omega_{i\infty}^{-1}}.$$

Since the nominator and denominator have the same homogeneity, the limit inferior remains unchanged if $\boldsymbol{\eta} = (\eta_1, \ldots, \eta_{n+1})$ has unit length, $\|\boldsymbol{\eta}\|_{\mathbb{R}^{n+1}} = 1$ (using the Euclidean norm). We infer from $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0 = \widehat{\mathbb{Q}}\boldsymbol{\omega}_\infty$ that $\widehat{\mathbb{Q}}\boldsymbol{\eta} = 0$. Hence, we have $\delta = 0$ if and only if there exists a vector $\boldsymbol{\eta} \in \mathbb{R}^{n+1}$ satisfying $\|\boldsymbol{\eta}\|_{\mathbb{R}^{n+1}} = 1$, $\widehat{\mathbb{Q}}\boldsymbol{\eta} = 0$, and

$$\sum_{i=1}^{n+1}(\mu_i^a - \nu_i^a)\frac{\eta_i}{\omega_{i\infty}} = 0 \quad \text{for all } a = 1, \ldots, N.$$

The last identity implies that the vector $\boldsymbol{\eta}/\boldsymbol{\omega}_\infty := (\eta_1/\omega_{1\infty}, \ldots, \eta_{n+1}/\omega_{n+1,\infty})^\top$ belongs to the kernel of $\mathbb{P}^\top$, where

$$\mathbb{P} = \left(\boldsymbol{\nu}^a - \boldsymbol{\mu}^a\right)_{a=1,\ldots,N} \in \mathbb{R}^{(n+1)\times N}.$$

Since the rows of $\mathbb{Q}$ form a basis of the Wegscheider matrix $\mathbb{W} = (\boldsymbol{\beta}^a - \boldsymbol{\alpha}^a)_{a=1,\ldots,N}$, and taking into account definition (22) of $\boldsymbol{\mu}^a$ and $\boldsymbol{\nu}^a$, we see that the columns of the matrix

$$\mathbb{Q}^* := \begin{pmatrix} \mathbb{Q}^\top & \mathbf{1}_n \\ \mathbf{0} & 1 \end{pmatrix}$$

form a basis of $\ker(\mathbb{P}^\top)$. We deduce that there exists $\boldsymbol{\rho} \in \mathbb{R}^{n+1}$ such that $\boldsymbol{\eta}/\boldsymbol{\omega}_\infty = \mathbb{Q}^*\boldsymbol{\rho}$ or, equivalently, $\boldsymbol{\eta} = \mathbb{D}\mathbb{Q}^*\boldsymbol{\rho}$, where $\mathbb{D} = \mathrm{diag}(\omega_{1\infty}, \ldots, \omega_{n+1,\infty})$. Hence, because of $\widehat{\mathbb{Q}}\boldsymbol{\eta} = 0$, we obtain $\widehat{\mathbb{Q}}\mathbb{D}\mathbb{Q}^*\boldsymbol{\rho} = 0$. The idea is now to prove that $\boldsymbol{\rho} = 0$, which implies that $\boldsymbol{\eta} = \mathbb{D}\mathbb{Q}^*\boldsymbol{\rho} = 0$, contradicting $\|\boldsymbol{\eta}\|_{\mathbb{R}^{n+1}} = 1$.

We claim that the matrix $\widehat{\mathbb{Q}}\mathbb{D}\mathbb{Q}^*$ is invertible. Indeed, setting $\mathbb{A}_\infty = \operatorname{diag}(\omega_{1\infty}, \ldots, \omega_{n\infty})$, we compute

$$\widehat{\mathbb{Q}}\mathbb{D}\mathbb{Q}^* = \begin{pmatrix} \mathbb{Q} & \mathbf{0} \\ \mathbf{1}^\top & -1 \end{pmatrix} \begin{pmatrix} \mathbb{A}_\infty & \mathbf{0} \\ \mathbf{0} & \omega_{n+1,\infty} \end{pmatrix} \begin{pmatrix} \mathbb{Q}^\top & \mathbf{1} \\ \mathbf{0} & 1 \end{pmatrix} = \begin{pmatrix} \mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top & \mathbb{Q}\mathbb{A}_\infty\mathbf{1} \\ \mathbf{1}^\top\mathbb{A}_\infty\mathbb{Q}^\top & \mathbf{1}^\top\mathbb{A}_\infty\mathbf{1} - \omega_{n+1,\infty} \end{pmatrix}.$$

Since $\mathbf{1}^\top\mathbb{A}_\infty\mathbf{1} = \sum_{i=1}^n \omega_{i\infty} = \omega_{n+1,\infty}$ (see Proposition 11), it follows that

$$\widehat{\mathbb{Q}}\mathbb{D}\mathbb{Q}^* = \begin{pmatrix} \mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top & \mathbb{Q}\mathbb{A}_\infty\mathbf{1} \\ \mathbf{1}^\top\mathbb{A}_\infty\mathbb{Q}^\top & 0 \end{pmatrix}.$$

We claim that the matrix $\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top$ is regular. Since $\mathbb{Q}$ has full rank, so is $\mathbb{Q}^\top$, and we infer for all $\boldsymbol{\xi} \in \mathbb{R}^m$ that

$$\left\langle \boldsymbol{\xi}, \mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top\boldsymbol{\xi} \right\rangle = \left\langle \boldsymbol{\xi}, \mathbb{Q}\mathbb{A}_\infty^{1/2}\mathbb{A}_\infty^{1/2}\mathbb{Q}^\top\boldsymbol{\xi} \right\rangle = \left\langle \mathbb{A}_\infty^{1/2}\mathbb{Q}^\top\boldsymbol{\xi}, \mathbb{A}_\infty^{1/2}\mathbb{Q}^\top\boldsymbol{\xi} \right\rangle \geqslant 0$$

with equality if and only if $\boldsymbol{\xi} = \mathbf{0}$. Hence, $\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top$ is regular. Together with the rule on the determinant of block matrices, this shows that

$$\det(\widehat{\mathbb{Q}}\mathbb{D}\mathbb{Q}^*) = \det(\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top)\det\left[0 - (\mathbf{1}^\top\mathbb{A}_\infty\mathbb{Q}^\top)(\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top)^{-1}(\mathbb{Q}\mathbb{A}_\infty\mathbf{1})\right].$$

As we already know that $\det(\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top) \neq 0$, it remains to verify that the second factor does not vanish. As the expression in the brackets $[\cdots]$ is a number, we need to show that

$$(\mathbf{1}^\top\mathbb{A}_\infty\mathbb{Q}^\top)(\mathbb{Q}\mathbb{A}_\infty\mathbb{Q}^\top)^{-1}(\mathbb{Q}\mathbb{A}_\infty\mathbf{1}) \neq 0. \tag{42}$$

The diagonal matrix $\mathbb{A}_\infty \in \mathbb{R}^{n\times n}$ has strictly positive diagonal elements. Therefore, (42) is equivalent to

$$(\mathbf{1}^\top\mathbb{A}_\infty^{1/2})(\mathbb{A}_\infty^{1/2}\mathbb{Q}^\top)\big((\mathbb{Q}\mathbb{A}_\infty^{1/2})(\mathbb{A}_\infty^{1/2}\mathbb{Q}^\top)\big)^{-1}(\mathbb{Q}\mathbb{A}_\infty^{1/2})(\mathbf{1}^\top\mathbb{A}_\infty^{1/2})^\top \neq 0.$$

We abbreviate the left-hand side by introducing $\boldsymbol{z} = \mathbf{1}^\top\mathbb{A}_\infty^{1/2} \in \mathbb{R}^{1\times n}$ and $\mathbb{X} = \mathbb{A}_\infty^{1/2}\mathbb{Q}^\top \in \mathbb{R}^{n\times m}$. Then (42) becomes

$$\boldsymbol{z}\mathbb{X}(\mathbb{X}^\top\mathbb{X})^{-1}\mathbb{X}^\top\boldsymbol{z}^\top \neq 0.$$

Since $\mathbb{X}$ is not a square matrix, we cannot invert it, but we may consider its Moore-Penrose generalized inverse $\mathbb{X}^\dagger$; see [37] or [39, Section 11.5] for a definition and properties. We compute

$$\begin{aligned}
\boldsymbol{z}\mathbb{X}(\mathbb{X}^\top\mathbb{X})^{-1}\mathbb{X}^\top\boldsymbol{z}^\top &= \boldsymbol{z}\mathbb{X}(\mathbb{X}^\top\mathbb{X})^\dagger\mathbb{X}^\top\boldsymbol{z}^\top && \text{[39, page 218]} \\
&= \boldsymbol{z}\mathbb{X}\mathbb{X}^\dagger(\mathbb{X}^\top)^\dagger\mathbb{X}^\top\boldsymbol{z}^\top && \text{[37, Lemma 1.5]} \\
&= \boldsymbol{z}\mathbb{X}\mathbb{X}^\dagger(\mathbb{X}^\dagger)^\top\mathbb{X}^\top\boldsymbol{z}^\top && \text{[39, Prop. 11.5]} \\
&= \boldsymbol{z}(\mathbb{X}\mathbb{X}^\dagger)(\mathbb{X}\mathbb{X}^\dagger)^\top\boldsymbol{z}^\top && \text{[37, Lemma 1.5]} \\
&= \|(\mathbb{X}\mathbb{X}^\dagger)^\top\boldsymbol{z}^\top\|_{\mathbb{R}^n}^2.
\end{aligned}$$

Consequently, (42) holds if and only if $(\mathbb{X}\mathbb{X}^\dagger)^\top\boldsymbol{z}^\top \neq 0$ or $\boldsymbol{z}^\top \notin \ker((\mathbb{X}\mathbb{X}^\dagger)^\top)$. Now, it holds that

$$\ker\big((\mathbb{X}\mathbb{X}^\dagger)^\top\big) = \ker\big((\mathbb{X}^\dagger)^\top\mathbb{X}^\top\big) = \ker\big((\mathbb{X}^\top)^\dagger\mathbb{X}^\top\big) = \ker(\mathbb{X}^\top),$$

where the last step follows from [39, page 219]. We infer that $\boldsymbol{z}^\top \notin \ker((\mathbb{X}\mathbb{X}^\dagger)^\top)$ if and only if $\mathbb{A}_\infty^{1/2}\mathbf{1} = \boldsymbol{z}^\top \notin \ker(\mathbb{X}^\top) = \ker(\mathbb{Q}\mathbb{A}_\infty^{1/2})$, which is equivalent to

$$0 \neq (\mathbb{Q}\mathbb{A}_\infty^{1/2})(\mathbb{A}_\infty^{1/2}\mathbf{1}) = \mathbb{Q}\mathbb{A}_\infty\mathbf{1} = \mathbb{Q}\boldsymbol{\omega}'_\infty,$$

and this property holds true since $\mathbb{Q}\boldsymbol{\omega}'_\infty = \boldsymbol{M}^0 \neq 0$. This proves that (42) holds. As mentioned before, this implies that $\boldsymbol{\rho} = 0$ and consequently $\boldsymbol{\eta} = 0$, which contradicts the fact that $\boldsymbol{\eta}$ has unit length. We conclude that $\delta > 0$ (defined in Lemma 24) and $\lambda > 0$, finishing the proof. □

We now provide the technical computations needed in Lemma 21.

Lemma 24. *Let $\boldsymbol{\omega}_\infty$ be a positive detailed-balanced equilibrium constructed in Proposition 11. It holds that*

$$\delta := \liminf_{\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}}=\widehat{\boldsymbol{M}}^0,\,\overline{\boldsymbol{\omega}}\to\boldsymbol{\omega}_\infty} \frac{\sum_{a=1}^N \left\{(k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\right\}^2}{\sum_{i=1}^{n+1}\left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2}\right)^2}$$
$$= \frac{1}{2}\liminf_{\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}}=\widehat{\boldsymbol{M}}^0,\,\overline{\boldsymbol{\omega}}\to\boldsymbol{\omega}_\infty} \frac{\sum_{a=1}^N k_f^a\boldsymbol{\omega}_\infty^{\boldsymbol{\mu}^a}\left\{\sum_{i=1}^{n+1}(\mu_i^a - \nu_i^a)(\overline{\omega_i} - \omega_{i\infty})\omega_{i\infty}^{-1}\right\}^2}{\sum_{i=1}^{n+1}(\overline{\omega_i} - \omega_{i\infty})^2\omega_{i\infty}^{-1}}.$$

Proof. We denote by

$$D_1(\overline{\boldsymbol{\omega}}) = \sum_{a=1}^N \left((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\right)^2,$$
$$D_2(\overline{\boldsymbol{\omega}}) = \sum_{i=1}^{n+1}\left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2}\right)^2$$

the nominator and denominator of the definition of δ, respectively. We linearize both expressions around $\boldsymbol{\omega}_\infty$,

$$\begin{aligned} D_i(\overline{\boldsymbol{\omega}}) &= D_i(\boldsymbol{\omega}_\infty) + \nabla D_i(\boldsymbol{\omega}_\infty)\cdot(\overline{\boldsymbol{\omega}} - \boldsymbol{\omega}_\infty) \\ &\quad + \frac{1}{2}(\overline{\boldsymbol{\omega}} - \boldsymbol{\omega}_\infty)^\top\nabla^2 D_i(\boldsymbol{\omega}_\infty)(\overline{\boldsymbol{\omega}} - \boldsymbol{\omega}_\infty) + o(|\overline{\boldsymbol{\omega}} - \boldsymbol{\omega}_\infty|^2). \end{aligned} \tag{43}$$

Since $\boldsymbol{\omega}_\infty$ is a detailed-balanced equilibrium, it holds that $(k_f^a)^{1/2}\sqrt{\boldsymbol{\omega}_\infty}^{\boldsymbol{\mu}^a} = (k_b^a)^{1/2}\sqrt{\boldsymbol{\omega}_\infty}^{\boldsymbol{\nu}^a}$ for all $a = 1,\ldots,N$, implying that $D_1(\boldsymbol{\omega}_\infty) = 0$ and $\nabla D_1(\boldsymbol{\omega}_\infty) = 0$. Let $\partial_i = \partial/\partial\omega_i$. Then

$$\begin{aligned} &\partial_j\partial_i D_1(\overline{\boldsymbol{\omega}}) \\ &= \sum_{a=1}^N\bigg\{\partial_j\partial_i\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big) \\ &\quad + \partial_i\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)\partial_j\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)\bigg\}. \end{aligned}$$

The first term vanishes for $\overline{\boldsymbol{\omega}} = \boldsymbol{\omega}_\infty$, and for the second term we compute

$$\partial_i\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)$$

$$
\begin{aligned}
&= (k_f^a)^{1/2}\partial_i \prod_{k=1}^{n+1} \overline{\omega_k}^{\mu_k^a/2} - (k_b^a)^{1/2}\partial_i \prod_{k=1}^{n+1} \overline{\omega_k}^{\nu_k^a/2} \\
&= (k_f^a)^{1/2}\frac{\mu_i^a}{2}\frac{1}{\overline{\omega_i}} \prod_{k=1}^{n+1} \overline{\omega_k}^{\mu_k^a/2} - (k_b^a)^{1/2}\frac{\nu_i^a}{2}\frac{1}{\overline{\omega_i}} \prod_{k=1}^{n+1} \overline{\omega_k}^{\nu_k^a/2} \\
&= \frac{1}{2\overline{\omega_i}}\Big((k_f^a)^{1/2}\mu_i^a\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\nu_i^a\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big).
\end{aligned}
$$

Evaluating this expression at $\overline{\boldsymbol{\omega}} = \boldsymbol{\omega}_\infty$ and using $(k_f^a)^{1/2}\sqrt{\boldsymbol{\omega}_\infty}^{\boldsymbol{\mu}^a} = (k_b^a)^{1/2}\sqrt{\boldsymbol{\omega}_\infty}^{\boldsymbol{\nu}^a}$, it follows that

$$
\partial_i\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)\Big|_{\overline{\boldsymbol{\omega}}=\boldsymbol{\omega}_\infty} = \frac{1}{2}\frac{\mu_i^a-\nu_i^a}{\omega_{i\infty}}(k_f^a)^{1/2}\sqrt{\boldsymbol{\omega}_\infty}^{\boldsymbol{\mu}^a}.
$$

Consequently,

$$
\partial_j\partial_i D_1(\boldsymbol{\omega}_\infty) = \frac{1}{4}\sum_{a=1}^N k_f^a \boldsymbol{\omega}_\infty^{\boldsymbol{\mu}^a}\frac{\mu_i^a-\nu_i^a}{\omega_{i\infty}}\frac{\mu_j^a-\nu_j^a}{\omega_{j\infty}},
$$

and the quadratic term in the Taylor expansion becomes at the point $\boldsymbol{\omega}_\infty$

$$
\frac{1}{2}(\overline{\boldsymbol{\omega}}-\boldsymbol{\omega}_\infty)^\top\nabla^2 D_i(\boldsymbol{\omega}_\infty)(\overline{\boldsymbol{\omega}}-\boldsymbol{\omega}_\infty) = \frac{1}{8}\sum_{a=1}^N k_f^a\boldsymbol{\omega}_\infty^{\boldsymbol{\mu}^a}\bigg(\sum_{i=1}^{n+1}\frac{\mu_i^a-\nu_i^a}{\omega_{i\infty}}(\overline{\omega_i}-\omega_{i\infty})\bigg)^2.
$$

Similarly, $D_2(\boldsymbol{\omega}_\infty) = 0$, $\nabla D_2(\boldsymbol{\omega}_\infty) = 0$, and

$$
\frac{1}{2}(\overline{\boldsymbol{\omega}}-\boldsymbol{\omega}_\infty)^\top\nabla^2 D_2(\boldsymbol{\omega}_\infty)(\overline{\boldsymbol{\omega}}-\boldsymbol{\omega}_\infty) = \frac{1}{4}\sum_{i=1}^{n+1}\frac{(\overline{\omega_i}-\omega_{i\infty})^2}{\omega_{i\infty}}.
$$

We insert these expressions into (43) and compute $D_1(\overline{\boldsymbol{\omega}})/D_2(\overline{\boldsymbol{\omega}})$. The limit $\overline{\boldsymbol{\omega}} \to \boldsymbol{\omega}_\infty$ such that $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0$ then gives the conclusion. □

We are ready to prove the main result of this subsection.

Proposition 25 (Entropy entropy-production inequality; unequal homogeneities)**.** *Fix $\boldsymbol{M}^0 \in \mathbb{R}_+^m$ such that $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. Let $\boldsymbol{x}_\infty$ be the equilibrium constructed in Theorem 10. Assume that (36) holds and system (1)–(2) has no boundary equilibria. Then there exists a constant $\lambda > 0$, which is constructive up to a finite-dimensional inequality (in the sense of Remark 23), such that*

$$
D[\boldsymbol{x}] \geqslant \lambda E[\boldsymbol{x}|\boldsymbol{x}_\infty]
$$

for all functions $\boldsymbol{x} : \Omega \to \mathbb{R}_+^n$ having the same regularity as the corresponding solutions in Theorem 3 and satisfying $\mathbb{Q}\overline{\boldsymbol{c}} = \boldsymbol{M}^0$.

Proof. Lemma 15 shows that

$$
E[\boldsymbol{x}|\boldsymbol{x}_\infty] \leqslant C\sum_{i=1}^n\bigg(\int_\Omega\Big(c_i^{1/2}-\overline{c_i^{1/2}}\Big)^2 dz + \big(\overline{c_i}^{1/2}-c_{i\infty}^{1/2}\big)^2\bigg). \tag{44}
$$

The first sum is controlled by $D[\boldsymbol{x}]$ using Lemma 16 and the Poincaré inequality (with constant $C_P > 0$):

$$D[\boldsymbol{x}] \geqslant \sum_{i=1}^n \int_\Omega |\nabla c_i^{1/2}|^2 dz \geqslant C_p \sum_{i=1}^n \int_\Omega \big(c_i^{1/2} - \overline{c_i^{1/2}}\big)^2 dz.$$

The second sum on the right-hand side is estimated by combining estimate (39), Lemma 20, and Lemma 21:

$$D[\boldsymbol{x}] \geqslant C \sum_{i=1}^{n+1} \big(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2}\big)^2 \geqslant C \sum_{i=1}^n \big(\overline{c_i}^{1/2} - c_{i\infty}^{1/2}\big)^2.$$

Adding the previous two inequalities and using (44) then concludes the proof. □

3.6. **Proof of Theorem 1.** The starting point is the discrete entropy inequality (see Remark 7):

$$E[\boldsymbol{x}^k|\boldsymbol{x}_\infty] + \tau D[\boldsymbol{x}^k] + C\varepsilon\tau \sum_{i=1}^{n-1} \|w_i^k\|_{H^l(\Omega)}^2 \leqslant E[\boldsymbol{x}^{k-1}|\boldsymbol{x}_\infty].$$

Using the entropy-production inequality from Propositions 18 or 25, this becomes

$$E[\boldsymbol{x}^k|\boldsymbol{x}_\infty] \leqslant (1+\lambda\tau)^{-1} E[\boldsymbol{x}^{k-1}|\boldsymbol{x}_\infty]$$

and, by induction,

$$E[\boldsymbol{x}^k|\boldsymbol{x}_\infty] \leqslant (1+\lambda\tau)^{-k} E[\boldsymbol{x}^0|\boldsymbol{x}_\infty] = (1+\lambda\tau)^{-T/\tau} E[\boldsymbol{x}^0|\boldsymbol{x}_\infty].$$

Performing the limit $\tau \to 0$ or, equivalently, $k \to \infty$, we find that

$$E[\boldsymbol{x}(T)|\boldsymbol{x}_\infty] \leqslant \liminf_{k\to\infty} E[\boldsymbol{x}^k|\boldsymbol{x}_\infty] \leqslant e^{-\lambda T} E[\boldsymbol{x}^0|\boldsymbol{x}_\infty].$$

Clearly, this inequality also holds for $t \in (0,T)$ instead of T. Then, by the Csiszár–Kullback–Pinsker inequality in Lemma 17, with constant $C_{\mathrm{CKP}} > 0$,

$$\sum_{i=1}^n \|x_i(t) - x_{i\infty}\|_{L^1(\Omega)}^2 \leqslant \frac{e^{-\lambda t}}{C_{\mathrm{CKP}}} \int_\Omega h(\boldsymbol{\rho}'(0)) dz.$$

As x_i is bounded in $L^\infty(0,\infty;L^\infty(\Omega))$, we derive the convergence in L^p for $1 \leqslant p < \infty$ from an interpolation argument

$$\begin{aligned}\sum_{i=1}^n \|x_i(t) - x_{i\infty}\|_{L^p(\Omega)} &\leqslant \sum_{i=1}^n \|x_i(t) - x_{i\infty}\|_{L^\infty(\Omega)}^{1-1/p} \|x_i(t) - x_{i\infty}\|_{L^1(\Omega)}^{1/p} \\ &\leqslant Ce^{-\lambda t/(2p)}, \quad t > 0,\end{aligned}$$

which concludes the proof.

4. Example: a specific reaction

As mentioned in Remark 23, the rate of convergence to equilibrium is generally not constructive since the finite-dimensional inequality (41) is proved by a nonconstructive contradiction argument. The derivation of a constructive constant for this inequality seems to be a challenging problem, which goes beyond the scope of this paper. In this section, we show that, potentially in any specific system, the finite-dimensional inequality (41) can be proved in a constructive way and thus gives the exponential decay with constructive constant. More specifically, we consider the single reversible reaction

$$A_1 + A_2 \leftrightharpoons A_3.$$

We assume for simplicity that the forward and backward reaction constants equal one. Furthermore, $|\Omega| = 1$. The corresponding system reads as

$$\begin{aligned} \partial_t\rho_1 + \operatorname{div}\boldsymbol{j}_1 &= r_1(\boldsymbol{x}) = -M_1(x_1x_2 - x_3), \\ \partial_t\rho_2 + \operatorname{div}\boldsymbol{j}_2 &= r_2(\boldsymbol{x}) = -M_2(x_1x_2 - x_3), \\ \partial_t\rho_3 + \operatorname{div}\boldsymbol{j}_3 &= r_3(\boldsymbol{x}) = +M_3(x_1x_2 - x_3), \end{aligned} \tag{45}$$

We conclude from total mass conservation $r_1 + r_2 + r_3 = 0$, that $M_1 + M_2 = M_3$. There are two (formal) conservation laws. The first one follows from

$$\frac{d}{dt}\int_\Omega \big(c_1(t) + c_3(t)\big)dz = \frac{d}{dt}\int_\Omega \left(\frac{\rho_1(t)}{M_1} + \frac{\rho_3(t)}{M_3}\right)dz = 0,$$

leading to

$$\overline{c_1}(t) + \overline{c_3}(t) = M_{13} := \overline{c_1^0} + \overline{c_3^0},$$

where $\overline{c_i^0} = \overline{\rho_i^0}/M_i = \int_\Omega \rho_i^0 dz/M_i$. The second conservation law reads as

$$\overline{c_2}(t) + \overline{c_3}(t) = M_{23} := \overline{c_2^0} + \overline{c_3^0}.$$

The matrix $\mathbb{Q}$ in this case is

$$\mathbb{Q} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix},$$

and we can choose $\boldsymbol{\zeta} = (M_1, M_2)$ since the conservation of total mass, $M_1 + M_2 = M_3$, gives $\boldsymbol{\zeta}\mathbb{Q} = (M_1, M_2, M_3) = \boldsymbol{M}^\top$. The initial mass vector $\boldsymbol{M}^0 = (M_{13}, M_{23})^\top$ satisfies $\boldsymbol{\zeta}\boldsymbol{M}^0 = M_1M_{13} + M_2M_{23} = 1$. It is not difficult to check that the system is detailed balanced and possesses no boundary equilibria, and thus, for any fixed masses $M_{13} > 0$, $M_{23} > 0$, there exists a unique positive detailed-balanced equilibrium $\boldsymbol{x}_\infty = (x_{1\infty}, x_{2\infty}, x_{3\infty})^\top \in (0,1)^3$ satisfying

$$\begin{aligned} &x_{1\infty}x_{2\infty} = x_{3\infty}, \quad x_{1\infty} + x_{2\infty} + x_{3\infty} = 1, \\ &c_{1\infty} + c_{3\infty} = M_{13}, \quad c_{2\infty} + c_{3\infty} = M_{23}, \end{aligned} \tag{46}$$

where $c_{i\infty} = c_\infty x_{i\infty}$ and $c_\infty = (M_1x_{1\infty} + M_2x_{2\infty} + M_3x_{3\infty})^{-1}$. We claim that we can prove Lemma 21 with a constructive constant. More precisely, we show the following result.

Lemma 26. *There exists a* constructive constant $C_0 > 0$*, only depending on* $c_{i\infty}$ *and the upper bounds of* $\overline{c_i}$ $(i = 1, 2, 3)$*, such that*

$$\left(\sqrt{\overline{c_1}}\sqrt{\overline{c_2}} - \sqrt{\overline{c_3}}\sqrt{\overline{c}}\right)^2 \geqslant C_0 \sum_{i=1}^{3} \left(\sqrt{\overline{c_i}} - \sqrt{c_{i\infty}}\right)^2 \tag{47}$$

for all nonnegative numbers $\overline{c_i}$ *and* $\overline{c}$ *satisfying*

$$\begin{aligned} \overline{c_1} + \overline{c_3} &= M_{13} = c_{1\infty} + c_{3\infty}, \\ \overline{c_2} + \overline{c_3} &= M_{23} = c_{2\infty} + c_{3\infty}, \\ \overline{c_1} + \overline{c_2} + \overline{c_3} &= \overline{c}. \end{aligned} \tag{48}$$

Proof. We introduce new variables $\mu_1, \mu_2, \mu_3, \eta \in [-1, \infty)$ by

$$\overline{c_i} = c_{i\infty}(1 + \mu_i)^2 \quad \text{for } i = 1, 2, 3, \quad \overline{c} = c_\infty(1 + \eta)^2,$$

recalling that $c_\infty = c_{1\infty} + c_{2\infty} + c_{3\infty}$. The uniform bounds for $\overline{c_i}$ show that there exists a constant $\mu_{\max} > 0$ such that $|\mu_i| \leqslant \mu_{\max}$ for $i = 1, 2, 3$. Then the left-hand side of (47) can be formulated as

$$\begin{aligned} \left(\sqrt{\overline{c_1}}\sqrt{\overline{c_2}} - \sqrt{\overline{c_3}}\sqrt{\overline{c}}\right)^2 &= \left(c_{1\infty}^{1/2} c_{2\infty}^{1/2}(1 + \mu_1)(1 + \mu_2) - c_{3\infty}^{1/2} c_\infty^{1/2}(1 + \mu_3)(1 + \eta)\right)^2 \\ &= c_{1,\infty} c_{2\infty}\left((1 + \mu_1)(1 + \mu_2) - (1 + \mu_3)(1 + \eta)\right)^2, \end{aligned}$$

where we have used $c_{1\infty}c_{2\infty} = x_{1\infty}x_{2\infty}c_\infty^2 = x_{3\infty}c_\infty^2 = c_{3\infty}c_\infty$, which follows from $x_{i\infty} = c_{i\infty}/c_\infty$ and the first equation in (46). Furthermore, the right-hand side of (47) is estimated from above by

$$\sum_{i=1}^{3} \left(\sqrt{\overline{c_i}} - \sqrt{c_{i\infty}}\right)^2 = \sum_{i=1}^{3} c_{i\infty}\mu_i^2 \leqslant \max_{i=1,2,3} c_{i\infty} \sum_{i=1}^{3} \mu_i^2.$$

Therefore, it remains to prove the inequality

$$\left((1 + \mu_1)(1 + \mu_2) - (1 + \mu_3)(1 + \eta)\right)^2 \geqslant C^* \sum_{i=1}^{3} \mu_i^2 \tag{49}$$

for some constructive constant $C^* > 0$.

In terms of the new variables μ_i, the conservation laws in (48) can be written as

$$\begin{aligned} c_{1\infty}(\mu_1^2 + 2\mu_1) + c_{3\infty}(\mu_3^2 + 2\mu_3) &= 0, \\ c_{2\infty}(\mu_2^2 + 2\mu_2) + c_{3\infty}(\mu_3^2 + 2\mu_3) &= 0. \end{aligned} \tag{50}$$

Together with the last equation in (48), we obtain

$$c_{1\infty}(\mu_1^2 + 2\mu_1) = c_{2\infty}(\mu_2^2 + 2\mu_2) = c_\infty(\eta^2 + 2\eta). \tag{51}$$

Since $\mu_i \geqslant -1$ and $\eta \geqslant -1$, we deduce from (50) and (51) that μ_1, μ_2, and η always have the same sign and μ_3 has the opposite sign. We consider therefore two cases:

Case 1: μ_1, μ_2, $\eta \geqslant 0$ *and* $\mu_3 \leqslant 0$. Since $\eta^2 + 2\eta \geqslant 0$ and $c_\infty = c_{1\infty} + c_{2\infty} + c_{3\infty}$, it follows from (51) that

$$c_{1\infty}(\mu_1^2 + 2\mu_1) = c_\infty(\eta^2 + 2\eta) \geqslant c_{1\infty}(\eta^2 + 2\eta)$$

and hence $\mu_1 \geqslant \eta$ (as $z \mapsto z^2 + 2z$ is increasing on $[-1, \infty)$). Similarly, we find that $\mu_2 \geqslant \eta$. Therefore,

$$(1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta) = (\mu_1 - \eta) + \mu_2 + \mu_1\mu_2 + (-\mu_3) + (-\mu_3)\eta \geqslant 0.$$

Taking the square of this equation, it follows that

$$\begin{aligned}\big((1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta)\big)^2 &\geqslant \big((\mu_1 - \eta) + \mu_2 + (-\mu_3)\big)^2 \\ &\geqslant (\mu_1 - \eta)^2 + \mu_2^2 + (-\mu_3)^2 \geqslant \mu_2^2 + \mu_3^2.\end{aligned}$$

Exchanging the roles of μ_1 and μ_2, we find that

$$\big((1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta)\big)^2 \geqslant \mu_1^2 + \mu_3^2.$$

Adding these inequalities, we have proved (49) with $C^* = \frac{1}{2}$.

Case 2: μ_1, μ_2, $\eta \leqslant 0$ and $\mu_3 \geqslant 0$. Because of $\eta^2 + 2\eta \leqslant 0$, we have

$$c_{1\infty}(\mu_1^2 + 2\mu_1) = c_\infty(\eta^2 + 2\eta) \leqslant c_{1\infty}(\eta^2 + 2\eta),$$

which yields $\mu_1 \leqslant \eta$. Similarly, $\mu_2 \leqslant \eta$. A similar argument as in case 1 leads to

$$(1+\mu_3)(1+\eta) - (1+\mu_1)(1+\mu_2) = \mu_3(1+\eta) + (\eta - \mu_1) + (-\mu_2)(1+\mu_1) \geqslant 0.$$

Hence, taking the square,

$$\begin{aligned}\big((1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta)\big)^2 &\geqslant \big(\mu_3(1+\eta) + (\eta - \mu_1) + (-\mu_2)(1+\mu_1)\big)^2 \\ &\geqslant \mu_3^2(1+\eta)^2. \end{aligned} \tag{52}$$

We deduce from (51) that

$$\begin{aligned}c_\infty(1+\eta)^2 = c_\infty + c_\infty(\eta^2 + 2\eta) &= c_\infty + c_{1\infty}(\mu_1^2 + 2\mu_1) \\ &= c_{2\infty} + c_{3\infty} + c_{1\infty}(1+\mu_1)^2.\end{aligned}$$

Consequently, $(1+\eta)^2 \geqslant (c_{2\infty} + c_{3\infty})/c_\infty$ and (52) becomes

$$\big((1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta)\big)^2 \geqslant \frac{c_{2\infty} + c_{3\infty}}{c_\infty}\mu_3^2. \tag{53}$$

We infer from $c_{3\infty}(\mu_3^2 + 2\mu_3) = c_{1\infty}(\mu_1^2 + 2\mu_1)$ (see (51)) that

$$\mu_3 = \frac{c_{1\infty}(\mu_1 + 2)}{c_{3\infty}(\mu_3 + 2)}(-\mu_1) \geqslant \frac{c_{1\infty}}{c_{3\infty}(\mu_{\max} + 2)}(-\mu_1) \geqslant 0,$$

where $\mu_{\max} = \max_{i=1,2,3} \mu_i$. Taking the square gives

$$\mu_3^2 \geqslant \frac{c_{1\infty}^2}{c_{3\infty}^2(\mu_{\max} + 2)^2}\mu_1^2,$$

and similarly,

$$\mu_3^2 \geqslant \frac{c_{2\infty}^2}{c_{3\infty}^2(\mu_{\max} + 2)^2}\mu_2^2.$$

We employ these bounds in (53) to obtain

$$\big((1+\mu_1)(1+\mu_2) - (1+\mu_3)(1+\eta)\big)^2 \geqslant C^*(\mu_1^2 + \mu_2^2 + \mu_3^2),$$

where

$$C^* = \frac{1}{3}\min\left\{\frac{c_{2\infty}+c_{3\infty}}{c_\infty}, \frac{c_{1\infty}^2}{c_{3\infty}^2(\mu_{\max}+2)^2}, \frac{c_{2\infty}^2}{c_{3\infty}^2(\mu_{\max}+2)^2}\mu_2^2\right\}.$$

This proves (49) and completes the proof. □

5. Convergence to equilibrium for complex-balanced systems

One of the main assumptions of this paper is the detailed-balanced condition (5). This condition was used extensively in the thermodynamic community and it leads to a natural entropy functional that is the core tool for the global existence analysis and the large-time asymptotics. However, the detailed-balance condition requires that the reaction system is reversible which is quite restrictive. In chemical reaction network theory, it is well known that there exists a much larger class of reaction systems, namely so-called *complex-balanced systems* which also exhibits an entropy structure; see, e.g., [13, 18, 20] for reaction-diffusion systems. In this section, we show that the global existence and large-time behavior results can be extended to systems satisfying the complex-balanced condition. We only highlight the differences of the proofs and present full proofs only when necessary.

Consider n constitutents A_i reacting in the following N reactions,

$$y_{1,a}A_1 + \cdots + y_{n,a}A_n \xrightarrow{k^a} y'_{1,a}A_1 + \cdots + y'_{n,a}A_n \quad \text{for } a = 1,\ldots,N,$$

where $k^a > 0$ is the reaction rate constant and $y_{i,a}$, $y'_{i,a} \in \{0\}\cup[1,\infty)$ are the stoichiometric coefficients. We set $\boldsymbol{y}_a = (y_{1,a},\ldots,y_{n,a})$ and $\boldsymbol{y}'_a = (y'_{1,a},\ldots,y'_{n,a})$. We denote by $\mathcal{C} = \{\boldsymbol{y}_a, \boldsymbol{y}'_a\}_{a=1,\ldots,N}$ the set of all complexes. We use as in [13] the convention that the primed complexes $\boldsymbol{y}'_a \in \mathcal{C}$ denote the product of the ath reaction, and the unprimed complexes $\boldsymbol{y}_a \in \mathcal{C}$ denote the reactant. Note that it may happen that $\boldsymbol{y}_a = \boldsymbol{y}'_b$ for some a, $b \in \{1,\ldots,N\}$. This means that a complex can be a reactant for one reaction and a product for another reaction.

The Maxwell–Stefan diffusion system consists of equations (1), (3), and

$$r_i(\boldsymbol{x}) = M_i \sum_{a=1}^N k^a(y'_{i,a} - y_{i,a})\boldsymbol{x}^{\boldsymbol{y}_a} \quad \text{with } \boldsymbol{x}^{\boldsymbol{y}_a} = \prod_{i=1}^n x_i^{y_{i,a}}. \tag{54}$$

We assume again the conservation of total mass, expressed as

$$\sum_{i=1}^n r_i(\boldsymbol{x}) = 0.$$

Definition 1 (Complex-balance condition)**.** *A homogeneous equilibrium state $\boldsymbol{x}_\infty$ is called a* complex-balanced equilibrium *if for any $\boldsymbol{y} \in \mathcal{C}$, it holds that*

$$\sum_{a\in\{1,\ldots,N\}:\boldsymbol{y}_a=\boldsymbol{y}} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} = \sum_{b\in\{1,\ldots,N\}:\boldsymbol{y}'_b=\boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b}. \tag{55}$$

Roughly speaking, $\boldsymbol{x}_\infty$ is a complex-balanced equilibrium if for any complex $\boldsymbol{y} \in \mathcal{C}$ the total input into each complex balances the total flow out of the complex. The condition is weaker than detailed balance since it does not require each step in the forward reaction to be balanced by a reverse reaction. We say that system (1), (3), and (54) is a complex-balanced system if it admits a positive complex-balanced equilibrium. Already Boltzmann studied complex-balanced systems in the context of kinetic theory, under the name of semi-detailed balance [2]. For chemical reaction systems, this condition was systematically studied in [17, 27].

The existence of global weak solutions to (1), (3), and (54) follows as in Section 2. We just have to verify that Lemma 6 also holds in the case of the reaction terms (54).

Lemma 27. *Let $\boldsymbol{x}_\infty$ be a positive complex-balanced equilibrium and let the entropy variable $\boldsymbol{w} \in \mathbb{R}^{n-1}$ be defined by $w_i = \partial h/\partial \rho_i$, $i = 1, \ldots, n-1$, where h is given by (8). Then for all $\boldsymbol{x} \in \mathbb{R}^n$, considered as a function of $\boldsymbol{w}$,*

$$\sum_{i=1}^{n-1} r_i(\boldsymbol{x}) w_i \leqslant 0.$$

Proof. By (18) and definition (54) of r_i, we compute

$$\begin{aligned}
\sum_{i=1}^{n-1} r_i(\boldsymbol{x}) w_i &= \sum_{i=1}^{n} \frac{r_i(\boldsymbol{x})}{M_i} \ln \frac{x_i}{x_{i\infty}} = \sum_{i=1}^{n}\sum_{a=1}^{N} k^a (y'_{i,a} - y_{i,a}) \boldsymbol{x}^{\boldsymbol{y}_a} \ln \frac{x_i}{x_{i\infty}} \\
&= \sum_{a=1}^{N} k^a \boldsymbol{x}^{\boldsymbol{y}_a} \ln \frac{\boldsymbol{x}^{\boldsymbol{y}'_a - \boldsymbol{y}}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a - \boldsymbol{y}}} \\
&= -\sum_{a=1}^{N} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \left\{ \frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} \ln \left(\frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} \Big/ \frac{\boldsymbol{x}^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}} \right) - \frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} + \frac{\boldsymbol{x}^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}} \right\} \\
&\quad - \sum_{a=1}^{N} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \left(\frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} - \frac{\boldsymbol{x}^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}} \right).
\end{aligned}$$

The expression in the curly brackets $\{\cdots\}$ equals $\Psi(\boldsymbol{x}^{\boldsymbol{y}_a}/\boldsymbol{x}_\infty^{\boldsymbol{y}_a}, \boldsymbol{x}^{\boldsymbol{y}'_a}/\boldsymbol{x}_\infty^{\boldsymbol{y}'_a})$, where $\Psi(x,y) = x\ln(x/y) - x + y$ is a nonnegative function. Hence, the first expression on the right-hand side is nonpositive. We claim that the second expression vanishes. Then $\sum_{i=1}^{n-1} r_i(\boldsymbol{x}) w_i \leqslant 0$. Indeed, by the complex-balanced condition (55),

$$\begin{aligned}
\sum_{a=1}^{N} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \left(\frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} - \frac{\boldsymbol{x}^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}} \right) &= \sum_{\boldsymbol{x} \in \mathcal{C}} \left(\sum_{a:\boldsymbol{y}_a = \boldsymbol{y}} k^a \boldsymbol{x}^{\boldsymbol{y}_a} - \sum_{b:\boldsymbol{y}'_b = \boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} \frac{\boldsymbol{x}^{\boldsymbol{y}'_b}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_b}} \right) \\
&= \sum_{\boldsymbol{y} \in \mathcal{C}} \left(\boldsymbol{x}^{\boldsymbol{y}} \sum_{a:\boldsymbol{y}_a = \boldsymbol{y}} k^a - \frac{\boldsymbol{x}^{\boldsymbol{y}}}{\boldsymbol{x}_\infty^{\boldsymbol{y}}} \sum_{b:\boldsymbol{y}'_b = \boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} \right) \\
&= \sum_{\boldsymbol{y} \in \mathcal{C}} \frac{\boldsymbol{x}^{\boldsymbol{y}}}{\boldsymbol{x}_\infty^{\boldsymbol{y}}} \left(\sum_{a:\boldsymbol{y}_a = \boldsymbol{y}} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} - \sum_{b:\boldsymbol{y}'_b = \boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} \right) = 0.
\end{aligned}$$

This shows the claim and ends the proof. ∎

Next, we show the existence of a unique complex-balanced equilibrium. For this, we denote as before by $\mathbb{W} = (\boldsymbol{y}'_a - \boldsymbol{y}_a)_{a=1,\ldots,N} \in \mathbb{R}^{n\times N}$ the Wegscheider matrix, set $m = \dim(\ker \mathbb{W}) > 0$, and denote by $\mathbb{Q} \in \mathbb{R}^{m\times n}$ the matrix whose rows form a basis of $\ker(\mathbb{W}^\top)$. As in Section 3.1, the conservation laws are given by

$$\mathbb{Q}\overline{\boldsymbol{c}}(t) = \boldsymbol{M}^0 := \mathbb{Q}\overline{\boldsymbol{c}^0}, \quad t > 0,$$

and there exists $\boldsymbol{\zeta} \in \mathbb{R}^{1\times m}$ such that $\boldsymbol{\zeta}\mathbb{Q} = \boldsymbol{M}^\top$ and $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$.

Proposition 28 (Existence of a complex-balanced equilibrium)**.** *Let $\boldsymbol{M}^0 \in \mathbb{R}^m_+$ be an initial mass vector satisfying $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. Then there exists a unique positive complex-balanced equilibrium $\boldsymbol{x}_\infty \in \mathbb{R}^n_+$ satisfying* (55) *and*

$$\mathbb{Q}\boldsymbol{x}_\infty = \boldsymbol{M}^0 \sum_{i=1}^n M_i x_{i\infty}, \quad \sum_{i=1}^n x_{i\infty} = 1. \tag{56}$$

The proof follows from the case of detailed balance with the help of the following lemma.

Lemma 29. *Let $\boldsymbol{x}_\infty$ be a positive complex-balanced equilibrium. Then the following two statements are equivalent:*

(i) *The vector $\boldsymbol{x}_* \in \mathbb{R}^n_+$ is a complex-balanced equilibrium.*

(ii) *It holds for all $a = 1, \ldots, N$:*

$$\frac{\boldsymbol{x}_*^{\boldsymbol{y}_a}}{\boldsymbol{x}_*^{\boldsymbol{y}'_a}} = \frac{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}}.$$

Proof. Let (ii) hold. We compute

$$\begin{aligned}\sum_{a:\boldsymbol{y}_a=\boldsymbol{y}} k^a \boldsymbol{x}_*^{\boldsymbol{y}_a} &= \sum_{a:\boldsymbol{y}_a=\boldsymbol{y}} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \frac{\boldsymbol{x}_*^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} = \frac{\boldsymbol{x}_*^{\boldsymbol{y}}}{\boldsymbol{x}_\infty^{\boldsymbol{y}}} \sum_{a:\boldsymbol{y}_a=\boldsymbol{y}} k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \\ &= \frac{\boldsymbol{x}_*^{\boldsymbol{y}}}{\boldsymbol{x}_\infty^{\boldsymbol{y}}} \sum_{b:\boldsymbol{y}'_b=\boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} = \sum_{b:\boldsymbol{y}'_b=\boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} \frac{\boldsymbol{x}_*^{\boldsymbol{y}'_b}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_b}}.\end{aligned}$$

Taking into account (ii), it follows that

$$\sum_{a:\boldsymbol{y}_a=\boldsymbol{y}} k^a \boldsymbol{x}_*^{\boldsymbol{y}_a} = \sum_{b:\boldsymbol{y}'_b=\boldsymbol{y}} k^b \boldsymbol{x}_\infty^{\boldsymbol{y}_b} \frac{\boldsymbol{x}_*^{\boldsymbol{y}_b}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_b}} = \sum_{b:\boldsymbol{y}'_b=\boldsymbol{y}} k^b \boldsymbol{x}_*^{\boldsymbol{y}_b},$$

i.e., $\boldsymbol{x}_*$ is a complex-balanced equilibrium.

To show that (i) implies (ii), let $\boldsymbol{x}_*$ be a complex-balanced equilibrium. Then $r_i(\boldsymbol{x}_*) = 0$ for all $i = 1, \ldots, n$, and the proof of Lemma 27 shows that

$$0 = \sum_{i=1}^n \frac{r_i(\boldsymbol{x}_*)}{M_i} \ln \frac{x_{i*}}{x_{i\infty}} = -\sum_{a=1}^N k^a \boldsymbol{x}_\infty^{\boldsymbol{y}_a} \Psi\left(\frac{\boldsymbol{x}_*^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}}, \frac{\boldsymbol{x}_*^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}}\right),$$

where we recall that $\Psi(x, y) = x\ln(x/y) - x + y \geqslant 0$ and $\Psi(x, y) = 0$ if and only if $x = y$. The last property implies that $\boldsymbol{x}_*^{\boldsymbol{y}_a}/\boldsymbol{x}_\infty^{\boldsymbol{y}_a} = \boldsymbol{x}_*^{\boldsymbol{y}'_a}/\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}$, which is (ii). $\square$

We prove a result similar to that one stated in Lemma 19.

Lemma 30. *The vector* $\overline{\boldsymbol{\omega}} = (\overline{c_1}, \ldots, \overline{c_n}, \overline{c}) \in \mathbb{R}_+^{n+1}$ *satisfies*

$$\sqrt{\frac{\overline{\boldsymbol{\omega}}}{\boldsymbol{\omega}_\infty}}^{\boldsymbol{\mu}^a} = \sqrt{\frac{\overline{\boldsymbol{\omega}}}{\boldsymbol{\omega}_\infty}}^{\boldsymbol{\nu}^a} \quad \text{for all } a = 1, \ldots, N, \quad \widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0, \tag{57}$$

if and only if $\overline{\boldsymbol{\omega}} = \boldsymbol{\omega}_\infty = (c_{1\infty}, \ldots, c_{n\infty}, c_\infty)$ *and* $\boldsymbol{x}_\infty = (c_{1\infty}/c_\infty, \ldots, c_{n\infty}/c_\infty)$ *is a complex-balanced equilibrium. Here,* $c_\infty = \sum_{i=1}^n c_{i\infty}$ *and* $\widehat{\mathbb{Q}}$ *and* $\widehat{\boldsymbol{M}}^0$ *are defined in* (40).

Proof. Set $x_i = \overline{c_i}/\overline{c}$ for $i = 1, \ldots, n$. Then the first equation in (57) implies that, using definition (22) of $\boldsymbol{\mu}^a$ and $\boldsymbol{\nu}^a$,

$$\prod_{i=1}^n \frac{\overline{c_i}^{y_{i,a}}}{c_{i\infty}^{y_{i,a}}} = \prod_{i=1}^n \frac{\overline{c_i}^{y'_{i,a}}}{c_{i\infty}^{y'_{i,a}}} \frac{\overline{c}^{\gamma^a}}{c_\infty^{\gamma^a}}, \quad \text{where } \gamma^a = \sum_{i=1}^n (y_{i,a} - y'_{i,a}).$$

This is equivalent to

$$\frac{\boldsymbol{x}^{\boldsymbol{y}_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}_a}} = \frac{\boldsymbol{x}^{\boldsymbol{y}'_a}}{\boldsymbol{x}_\infty^{\boldsymbol{y}'_a}}.$$

We conclude from Lemma 29 that $\boldsymbol{x}$ is a complex-balanced equilibrium. Furthermore, we have

$$\sum_{i=1}^n M_i x_i = \frac{1}{\overline{c}} \sum_{i=1}^n M_i \overline{c_i} = \frac{1}{\overline{c}}.$$

Thus, we deduce from the conservation law $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0$ that

$$\mathbb{Q}\boldsymbol{x} = \frac{1}{\overline{c}}\boldsymbol{M}^0 = \boldsymbol{M}^0 \sum_{i=1}^n M_i x_i.$$

At this point, we can apply Proposition 28 to infer the existence of a unique vector $\boldsymbol{x} = \boldsymbol{x}_\infty$ which implies that $\overline{\boldsymbol{\omega}} = \boldsymbol{\omega}_\infty$. □

Finally, we show an inequality which is related to that one in Lemma 21.

Lemma 31. *There exists a nonconstructive constant* $C > 0$ *such that*

$$\sum_{a=1}^N \left(\sqrt{\frac{\overline{\boldsymbol{\omega}}}{\boldsymbol{\omega}_\infty}}^{\boldsymbol{\mu}^a} - \sqrt{\frac{\overline{\boldsymbol{\omega}}}{\boldsymbol{\omega}_\infty}}^{\boldsymbol{\nu}^a} \right)^2 \geqslant C \sum_{i=1}^{n+1} \left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2} \right)^2$$

for all $\overline{\boldsymbol{\omega}} \in \mathbb{R}_+^{n+1}$ *satisfying* $\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0$.

Proof. We proceed similarly as in the proofs of Lemmas 24 and 21. We need to show that

$$\lambda := \inf_{\overline{\boldsymbol{\omega}} \in \mathbb{R}_+^{n+1} : \widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0} \frac{\sum_{a=1}^N \left(\sqrt{\overline{\boldsymbol{\omega}}/\boldsymbol{\omega}_\infty}^{\boldsymbol{\mu}^a} - \sqrt{\overline{\boldsymbol{\omega}}/\boldsymbol{\omega}_\infty}^{\boldsymbol{\nu}^a} \right)^2}{\sum_{i=1}^{n+1} \left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2} \right)^2} > 0.$$

In view of Lemma 30 and the absence of boundary equilibria, it holds $\lambda > 0$ if and only if $\delta > 0$, where

$$\delta = \liminf_{\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}} = \widehat{\boldsymbol{M}}^0, \overline{\boldsymbol{\omega}} \to \boldsymbol{\omega}_\infty} \frac{\sum_{a=1}^N \left(\sqrt{\overline{\boldsymbol{\omega}}/\boldsymbol{\omega}_\infty}^{\boldsymbol{\mu}^a} - \sqrt{\overline{\boldsymbol{\omega}}/\boldsymbol{\omega}_\infty}^{\boldsymbol{\nu}^a} \right)^2}{\sum_{i=1}^{n+1} \left(\overline{\omega_i}^{1/2} - \omega_{i\infty}^{1/2} \right)^2}$$

$$= \liminf_{\widehat{\mathbb{Q}}\overline{\boldsymbol{\omega}}=\widehat{\boldsymbol{M}}^0,\, \overline{\boldsymbol{\omega}}\to\boldsymbol{\omega}_\infty} \frac{2\sum_{a=1}^{N}\big(\sum_{i=1}^{n+1}(y_{i,a}-y'_{i,a})(\overline{\omega_i}-\omega_{i\infty})\omega_{i\infty}^{-1}\big)^2}{\sum_{i=1}^{n+1}(\overline{\omega_i}-\omega_{i\infty})^2\omega_{i\infty}^{-1}}.$$

This follows from a Taylor expansion as in the proof of Lemma 24. Now, we can follow exactly the arguments in the proof of Lemma 21 to infer that $\delta > 0$ and consequently $\lambda > 0$, finishing the proof. □

The results in this subsection are sufficient to apply the proof of Theorem 1, thus leading to the following main theorem.

Theorem 32 (Convergence to equilibrium for complex-balanced systems)**.** *Let Assumptions (A1) and (A3) hold and let system (1), (54) be complex balanced. Fix an initial mass vector $\boldsymbol{M}^0 \in \mathbb{R}^m_+$ satisfying $\boldsymbol{\zeta}\boldsymbol{M}^0 = 1$. Then*

(i) *There exists a global bounded weak solution $\boldsymbol{\rho} = (\rho_1, \dots, \rho_n)^\top$ to (1), (3) with reaction terms (54) in the sense of Theorem 3.*

(ii) *There exists a unique positive complex-balanced equilibrium $\boldsymbol{x}_\infty \in \mathbb{R}^n_+$ satisfying (55) and (56).*

(iii) *Assume in addition that system (1), (54) has no boundary equilibria. Then there exist constants $C > 0$ and $\lambda > 0$, which are constructive up to a finite-dimensional inequality, such that if $\boldsymbol{\rho}^0$ satisfies additionally $\mathbb{Q}\int_\Omega \boldsymbol{c}^0 dz = \boldsymbol{M}^0$, the following exponential convergence to equilibrium holds*

$$\sum_{i=1}^{n} \|x_i(t) - x_{i\infty}\|_{L^p(\Omega)} \leqslant Ce^{-\lambda t/(2p)} E[\boldsymbol{x}^0|\boldsymbol{x}_\infty]^{1/(2p)}, \quad t > 0,$$

where $1 \leqslant p < \infty$, $x_i = \rho_i/(cM_i)$ with $c = \sum_{i=1}^n \rho_i/M_i$, and $E[\boldsymbol{x}|\boldsymbol{x}_\infty]$ is the relative entropy defined in (9), $\boldsymbol{\rho}$ is the solution constructed in (i)*, and $\boldsymbol{x}_\infty$ is constructed in* (ii)*.*

Appendix A. Proof of Lemma 20

The proof of Lemma 20 is partially inspired by the proof of Lemma 2.7 in [20]. We divide the proof into two steps, which are presented in Lemmas 33 and 34. For convenience, we set $W_i := \omega_i^{1/2}$ for $i = 1, \dots, n+1$ and use the notation

$$\boldsymbol{W} = (W_1, \dots, W_{n+1}), \quad \overline{\boldsymbol{W}} = (\overline{W}_1, \dots, \overline{W}_{n+1}).$$

Moreover, we define

$$\delta_i(x) = W_i(x) - \overline{W_i} = W_i(x) - \int_\Omega W_i dz, \quad x \in \Omega,\ i = 1, \dots, n+1.$$

Lemma 33. *There exists a constant $C > 0$ depending on Ω, n, N, k_f^a, and k_b^a ($a = 1, \dots, N$) such that*

$$\widetilde{D}[\boldsymbol{\omega}] \geqslant C\sum_{a=1}^{N}\Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \tag{58}$$

where $\widetilde{D}$ is defined in (39).

Proof. We use the elementary inequality $(x-y)\ln(x/y) \geqslant 4(\sqrt{x}-\sqrt{y})^2$ to obtain

$$\int_\Omega \big(k_f^a \boldsymbol{\omega}^{\boldsymbol{\mu}^a} - k_b^a \boldsymbol{\omega}^{\boldsymbol{\nu}^a}\big) \ln \frac{k_f^a \boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a \boldsymbol{\omega}^{\boldsymbol{\nu}^a}} dz \geqslant 4 \int_\Omega \big((k_f^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\nu}^a}\big)^2 dz.$$

This gives

$$\widetilde{D}[\boldsymbol{\omega}] \geqslant \sum_{i=1}^{n+1} \|\nabla W_i\|_{L^2(\Omega)}^2 + 4 \sum_{i=1}^{n+1} \big\|(k_f^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega}^2.$$

The Poincaré inequality

$$\|\nabla W_i\|_{L^2(\Omega)}^2 \geqslant C_P \|\delta_i\|_{L^2(\Omega)}^2$$

then shows that

$$\widetilde{D}[\boldsymbol{\omega}] \geqslant C_P \sum_{i=1}^{n+1} \|\delta_i\|_{L^2(\Omega)}^2 + 4 \sum_{i=1}^{n+1} \big\|(k_f^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega)}^2. \tag{59}$$

Let $L > 0$. We split Ω into the two domains

$$\Omega_L = \big\{x \in \Omega : |\delta_i(x)| \leqslant L \text{ for } i = 1, \ldots, n+1\big\}, \quad \Omega_L^c = \Omega \backslash \Omega_L.$$

By Taylor expansion, we may write $W_i^{\mu_i^a} = (\overline{W_i} + \delta_i)^{\mu_i^a} = \overline{W_i}^{\mu_i^a} + R_i^*(\overline{W_i}, \delta_i)\delta_i$, where R_i^* depends continuously on $\overline{W_i}$ and δ_i. Therefore,

$$\begin{aligned}
&\big\|(k_f^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega)}^2 \\
&\quad \geqslant \int_{\Omega_L} \bigg|(k_f^a)^{1/2} \prod_{i=1}^{n+1} (\overline{W_i} + \delta_i)^{\mu_i^a} - (k_b^a)^{1/2} \prod_{i=1}^{n+1} (\overline{W_i} + \delta_i)^{\nu_i^a}\bigg|^2 dz \\
&\quad = \int_{\Omega_L} \bigg|(k_f^a)^{1/2} \prod_{i=1}^{n+1} \big(\overline{W_i}^{\mu_i^a} + R_i^* \delta_i\big) - (k_b^a)^{1/2} \prod_{i=1}^{n+1} \big(\overline{W_i}^{\nu_i^a} + R_i^* \delta_i\big)\bigg|^2 dz \\
&\quad = \int_{\Omega_L} \bigg|(k_f^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a} + Q^* \sum_{i=1}^{n+1} \delta_i\bigg|^2 dz,
\end{aligned}$$

where Q^* depends continously on $R_1^*, \ldots, R_{n+1}^*$ and $\delta_1, \ldots, \delta_{n+1}$. With the inequalities $(x+y)^2 \geqslant \frac{1}{2}(x^2 - y^2)$ and $(\sum_{i=1}^{n+1} x_i)^2 \leqslant (n+1) \sum_{i=1}^{n+1} x_i^2$, we estimate

$$\begin{aligned}
&\big\|(k_f^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega)}^2 \\
&\quad \geqslant \frac{1}{2} |\Omega_L| \Big((k_f^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 - \int_{\Omega_L} (Q^*)^2 (n+1) \sum_{i=1}^{n+1} |\delta_i|^2 dz \\
&\quad \geqslant \frac{1}{2} |\Omega_L| \Big((k_f^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2} \overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 - C(L)(n+1) \sum_{i=1}^{n+1} \|\delta_i\|_{L^2(\Omega)}^2,
\end{aligned}$$

where we used the bounds $|\delta_i| \leqslant L$ in Ω_L and $\overline{W_i} \leqslant C$ in Ω to estimate Q^*. Summing over $a = 1, \ldots, N$, this gives

$$\begin{aligned}\sum_{a=1}^N \big\|(k_f^a)^{1/2}\boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega)}^2 &\geqslant \frac{1}{2}|\Omega_L| \sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\ &\quad - C(L)N(n+1)\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2. \end{aligned} \tag{60}$$

In Ω_L^c, we wish to estimate $\|\delta_i\|_{L^2(\Omega)}$ from below. For this, we observe that

$$\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \leqslant C.$$

Then, since $\sum_{i=1}^{n+1}|\delta_i| \geqslant L$ on Ω_L^c,

$$\begin{aligned}\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 &\geqslant \sum_{i=1}^{n+1}\int_{\Omega_L^c}|\delta_i|^2 dz \geqslant \frac{1}{n+1}\int_{\Omega_L^c}\Big(\sum_{i=1}^{n+1}|\delta_i|\Big)^2 dz \\ &\geqslant \frac{L^2|\Omega_L^c|}{n+1} \geqslant \frac{L^2|\Omega_L^c|}{(n+1)C}\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2. \end{aligned} \tag{61}$$

Inserting (60) and (61) into (59), it follows for any $\theta \in (0,1)$ that

$$\begin{aligned}\widetilde{D}[\boldsymbol{\omega}] &\geqslant C_P\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 + 4\theta\sum_{i=1}^{n+1}\big\|(k_f^a)^{1/2}\boldsymbol{W}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\boldsymbol{W}^{\boldsymbol{\nu}^a}\big\|_{L^2(\Omega)}^2 \\ &\geqslant \frac{C_P}{2}\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 + \frac{C_P}{2}\frac{L^2|\Omega_L^c|}{(n+1)C}\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\ &\quad + 2\theta|\Omega_L|\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 - 4\theta C(L)(n+1)\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 \\ &\geqslant C\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2, \end{aligned}$$

where we have chosen $\theta > 0$ sufficiently small in the last step. This finishes the proof. ☐

Lemma 34. *There exists a constant $C > 0$ depending on Ω, n, N, k_f^a, and k_b^a ($a = 1, \ldots, N$) such that*

$$\begin{aligned}\sum_{i=1}^{n+1}|\nabla\omega_i^{1/2}|^2 dz &+ \sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\ &\geqslant C\sum_{a=1}^N \Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2. \end{aligned} \tag{62}$$

Proof. It follows from

$$\|\delta_i\|_{L^2(\Omega)}^2 = \|W_i - \overline{W_i}\|_{L^2(\Omega)}^2 = \overline{\omega_i} - \overline{W_i}^2 = \big(\sqrt{\overline{\omega_i}} - \overline{W_i}\big)\big(\sqrt{\overline{\omega_i}} + \overline{W_i}\big)$$

that

$$\overline{W_i} = \sqrt{\overline{\omega_i}} - Z_i\|\delta_i\|_{L^2(\Omega)}, \quad \text{where } Z_i = \frac{\|\delta_i\|_{L^2(\Omega)}}{\sqrt{\overline{\omega_i}} + \overline{W_i}} \geqslant 0.$$

Since

$$Z_i^2 = \frac{\|\delta_i\|_{L^2(\Omega)}^2}{(\sqrt{\overline{\omega_i}} + \overline{W_i})^2} = \frac{\overline{\omega_i} - \overline{W_i}^2}{(\sqrt{\overline{\omega_i}} + \overline{W_i})^2} = \frac{\sqrt{\overline{\omega_i}} - \overline{W_i}}{\sqrt{\overline{\omega_i}} + \overline{W_i}} \leqslant 1,$$

we infer that $0 \leqslant Z_i \leqslant 1$.

We continue by performing a Taylor expansion:

$$\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} = \prod_{i=1}^{n+1}\big(\sqrt{\overline{\omega_i}} - Z_i\|\delta_i\|_{L^2(\Omega)}\big)^{\mu_i^a} = \prod_{i=1}^{n+1}\big(\sqrt{\overline{\omega_i}}^{\mu_i^a} + R_i^*\|\delta_i\|_{L^2(\Omega)}\big),$$

where R_i^* depends continuously on Z_i and $\|\delta_i\|_{L^2(\Omega)}$. Therefore, with another function S^* depending continuously on Z_i and $\|\delta_i\|_{L^2(\Omega)}$,

$$\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} = \sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} + S^*\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}.$$

This shows that

$$\begin{aligned}
&\sum_{a=1}^{N}\Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\
&\quad = \sum_{a=1}^{N}\bigg((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a} + \big((k_f^a)^{1/2} - (k_b^a)^{1/2}\big)S^*\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}\bigg)^2 \\
&\quad \geqslant \frac{1}{2}\sum_{a=1}^{N}\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2 - C(n,N)(S^*)^2\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2.
\end{aligned}$$

Then, by the Poincaré inequality with constant C_P, for some $\theta \in (0,1)$,

$$\begin{aligned}
&\sum_{i=1}^{n+1}|\nabla\omega_i^{1/2}|^2 dz + \sum_{a=1}^{N}\Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\
&\qquad \geqslant C_P\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 + \theta\sum_{a=1}^{N}\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2 \\
&\qquad \geqslant C_P\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2 + \frac{\theta}{2}\sum_{a=1}^{N}\Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2 \\
&\qquad\quad - \theta C(n,N)(S^*)^2\sum_{i=1}^{n+1}\|\delta_i\|_{L^2(\Omega)}^2
\end{aligned}$$

$$\geqslant \frac{\theta}{2}\sum_{a=1}^N \Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2.$$

The last step follows after choosing $\theta > 0$ sufficiently small. This is possible since S^* is bounded. The proof is complete. □

Proof of Lemma 20. Applying first (58) and then (62) leads to

$$\begin{aligned}
\widetilde{D}[\boldsymbol{\omega}] &\geqslant \frac{C}{2}\sum_{i=1}^{n+1}\int_\Omega |\nabla\omega_i^{1/2}|^2 dz \\
&\quad + \frac{C}{2}\bigg(\sum_{i=1}^{n+1}\int_\Omega |\nabla\omega_i^{1/2}|^2 dz + \sum_{a=1}^N\int_\Omega \big(k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a} - k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}\big)\ln\frac{k_f^a\boldsymbol{\omega}^{\boldsymbol{\mu}^a}}{k_b^a\boldsymbol{\omega}^{\boldsymbol{\nu}^a}}dz\bigg) \\
&\geqslant \frac{C}{2}\sum_{i=1}^{n+1}\int_\Omega |\nabla\omega_i^{1/2}|^2 dz + C\sum_{a=1}^N \Big((k_f^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\overline{\boldsymbol{W}}^{\boldsymbol{\nu}^a}\Big)^2 \\
&\geqslant C\sum_{a=1}^N \Big((k_f^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\mu}^a} - (k_b^a)^{1/2}\sqrt{\overline{\boldsymbol{\omega}}}^{\boldsymbol{\nu}^a}\Big)^2.
\end{aligned}$$

The proof is finished. □

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