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EXISTENCE OF GLOBAL SOLUTIONS OF MULTICOMPONENT REACTIVE TRANSPORT PROBLEMS WITH MASS ACTION KINETICS IN POROUS MEDIA

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Abstract We prove the existence and uniqueness of time-global solutions for multi-species multi-reaction advection-diffusion-dispersion problems with mass action kinetics in the space $W_p^{2,1}([0,T]\times\Omega)$. The reaction terms of mass action kinetics may contain polynomial expressions of arbitrarily high order. The difficulty to obtain an a priori estimate for the semilinar system of PDEs is tackled with a special Lyapunov function.

Keywords Existence of solutions, A priori estimate, Parabolic equations, Reactive transport, Mass action kinetics.

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1. Introduction

We consider a set of chemical species which are dissolved in a fluid and subject to chemical reactions. The fluid may flow through a porous medium. The species are transported through advective, diffusive and dispersive flow. An important application of this model is the reactive transport of species in the subsurface, i.e., in the groundwater, but setting the so-called porosity to unity, the results also apply to flow problems without porous media involved. The mathematical model consists of a system of semilinear partial differential equations (PDEs) for the concentrations of the species. They are coupled through nonlinear rate terms. In the following we will focus on reversible reaction rates of mass action type. Mass action kinetics is contained in most hydrogeochemical models (e.g., [4, 6, 9, 12], among many others) and thus plays an important role in particular in computational hydrogeochemistry. We do not limit the scope of the model by posing any restrictions on the number of species, the number of reactions, the dimension of the physical space, or the degree of nonlinearity of the rates.

An existence result for reactive transport with mass action kinetics is already given in [15] for the space $L^\infty(0,T;C^{2+\alpha}(\Omega))$. However, this result is restricted to purely diffusive transport (no advection) and homogeneous Neumann boundary conditions, and the assumption of strict positivity of solutions is made. Its derivation is based on the maximum principle. In the following we will derive a global existence result in the space $W_p^{2,1}([0,T]\times\Omega)$ (see Sec. 2.1), where transport through advection and dispersion with variable porosity of the medium is included, also

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dealing with more realistic flux boundary conditions. Working in a solution space of lower regularity than [15] leads to weaker assumptions on the data. Furthermore, we do not rely on an a priori assumption of strict positivity of solutions. The main difficulty is the high nonlinearity of the rate terms, which may consist of polynomial expressions of arbitrarily high order. We attack this problem with the method of a priori estimates, exploiting the structure of mass action rates. It turns out that, roughly speaking, it is sufficient that the data must come with such regularity that the corresponding *linear* advection-diffusion problem (i.e., without the nonlinear rate terms) admits a $W_p^{2,1}([0,T]\times\Omega)$ solution, which depends continuously on the right-hand side $f\in L^p([0,T]\times\Omega)$.

In [5] a result is given for multicomponent reactive flow with high order polynomial source terms, which in principal covers mass action kinetics; however, there a restrictive assumption called 'intermediate sum condition' is required. Roughly speaking, it means that the growth terms of at least one species have to be severely bounded. We do not pose any condition of this kind in the following.

The article is structured as follows. In Sec. 2.1 we give some definitions and we list our assumptions. In Sec. 2.2 and 2.3 we derive some results on the nonnegativity of solutions and we use a simple ODE model to briefly show how the structural information of a multicomponent mass action system can be exploited to derive an a priori estimate. In Sec. 3 we prove the existence and uniqueness of solutions of the PDE model, which is the main result of this paper, see Theorem 3.2. The most effort to obtain an a priori estimate has to be put into the proof of Lemma 3.1 which is the main step to derive the a priori estimates, first in $L^\infty(0,T;L^r(\Omega))$ (Lemma 3.2), then in $W_p^{2,1}([0,T]\times\Omega)$ (Lemma 3.3). In Sec. 4 we conclude with some remarks on the strategy applied.

2. Definitions, assumptions, and preliminary results

2.1. Definitions and assumptions

Let $T>0$ be a fixed time arbitrarily large. Let $\Omega\subset\mathbb{R}^n$ be a bounded domain with $n\geq 2$, and ν the outside unit normal vector on $\partial\Omega$. Let $Q_T=(0,T)\times\Omega$ be the space-time domain.

The sets of positive (nonnegative, respectively) real numbers are denoted by $\mathbb{R}_+=\{x\in\mathbb{R}\,|\,x>0\}$ and $\overline{\mathbb{R}}_+=\{x\in\mathbb{R}\,|\,x\geq 0\}$. $L^p_+(M):=\{u\in L^p(M)\,|\,u\geq 0 \text{ a.e.}\}$ is the set of nonnegative L^p-functions. Inequalities such as $u\geq 0$ are also used for expressions in $\mathbb{R}^n$, if they hold for each component. $|\cdot|_I$, $\langle\cdot,\cdot\rangle_I$ denote the Euclidian norm and inner product in $\mathbb{R}^I$. $\nabla=\nabla_x$ is the derivative of a scalar function with respect to the vector $x\in\Omega$; ∂_t, ∂_{x_i} denote partial differentiation. $D=D_x$ is the derivative (Jacobian) of a vector-valued function with respect to the vector $x\in\Omega$. The Banach space

$$W_p^{2,1}(Q_T)=\{u\,|\;\,u,\partial_t u,\partial_{x_i}u,\partial_{x_i}\partial_{x_j}u\in L^p(Q_T)\forall\, i,j=1,...,n\}$$

with the norm

$$\begin{aligned}&\|u\|_{W_p^{2,1}(Q_T)}\\ =\;&\Big(\|u\|^p_{L^p(Q_T)}+\|\partial_t u\|^p_{L^p(Q_T)}+\sum_{i=1}^n\|\partial_{x_i}u\|^p_{L^p(Q_T)}+\sum_{i,j=1}^n\|\partial_{x_i}\partial_{x_j}u\|^p_{L^p(Q_T)}\Big)^{1/p}\end{aligned}$$

is the space in which we will search for a solution $u_i \in W_p^{2,1}(Q_T)$. Vector-valued function spaces are denoted by a superscript indicating the dimension, that means for example $L^p(\Omega)^3 = L^p(\Omega)\times L^p(\Omega)\times L^p(\Omega)$; the corresponding norms are denoted by $\|v\|_{L^p(M)^I} = (\sum_{i=1}^I \|v_i\|_{L^p(M)}^p)^{1/p}$,
$\|v\|_{L^\infty(M)^I} = \max_{i=1...I}\|v_i\|_{L^\infty(M)}$; analogously we define $W_p^{2,1}(Q_T)^I$, etc.

By c we denote generic positive constants depending only on the problem parameters, but not on the solution, if not indicated otherwise.

Let us define the transport operator

$$Lu_i = \operatorname{div}(-A(t,x)\,\nabla u_i + q(t,x)u_i)$$

with $A(t,x)$ being a symmetric matrix which is uniformly elliptic, and with $q(t,x)\in\mathbb{R}^n$ being a given flow field (Darcy velocity field); $u = (u_1,...,u_I)^T$ is the vector of concentrations. We define $\mathcal{L}u = (Lu_1,...,Lu_I)$. Hence, we assume that all species are subject to the same advection and the same diffusion-dispersion. Note that in the community of multicomponent hydrogeosciences, models with species-independent diffusion-dispersion are common (a) since in most situations the (species-dependent) molecular diffusion is very small compared to the (species-independent) dispersion caused by the microscale, and (b) since it is exploited for high-performance numerical solution strategies for reactive transport problems (e.g., [2, 4, 9, 12] among many others). Many results on reactive problems with species-dependent diffusion, but usually (only) with two species and one or two specific reaction rates, can be found in the work of M. Pierre, e.g., [17].

The J reactions are of forward-backward type, also called reversible reactions,

$$s_{1j}^f X_1 + ... + s_{Ij}^f X_I \longleftrightarrow s_{1j}^b X_1 + ... + s_{Ij}^b X_I, \quad j = 1,...,J,$$

$s_{ij}^f, s_{ij}^b \geq 0$. The matrices $S^f = (s_{ij}^f)$, $S^b = (s_{ij}^b) \in \overline{\mathbb{R}}_+^{I\times J}$, $S = S^b - S^f$ are called stoichiometric matrices; the rate vector is $R(u) = R^f(u) - R^b(u)$. According to the mass action law the rates read

$$R_j^f(u) = k_j^f \prod_{i=1}^I u_i^{s_{ij}^f}, \quad R_j^b(u) = k_j^b \prod_{i=1}^I u_i^{s_{ij}^b}, \quad k_j^f, k_j^b > 0.$$

Note that the model admits of reactions such as $0 \to X_1+X_2$ or $X_1+2X_2 \to X_1+3X_2$. Hence, no strict physical mass conservation is included, i.e., no obvious a priori $L^1(\Omega)$-bound of the solution can be given easily.

The Darcy flow field q is related to the water content θ through the mass conservation equation

$$\partial_t\theta + \operatorname{div} q = 0. \tag{1}$$

We want to solve the following problem:

Problem 2.1. *Find $u \in W_p^{2,1}(Q_T)^I$ such that*

$$\partial_t(\theta u) + \mathcal{L}u = \theta\, S\, R(u) \tag{2}$$

with an initial condition

$$u(0) = u_0 \geq 0 \quad \text{on } \Omega$$

and an appropriate boundary condition. We may consider normal-diffusive-flux-zero boundary conditions (natural boundary conditions)

$$\langle \nu, A\nabla u_i\rangle_n = 0 \tag{3}$$

or flux boundary conditions

$$\langle \nu, A\nabla u_i - u_i q\rangle_n = b_i, \quad \text{with } b_i \geq 0, \tag{4}$$

*for $i = 1, ..., I$. To be as general as possible, we allow that (3) holds on $\partial\Omega_N$ and (4) holds on $\partial\Omega_F$, with a disjoint decomposition $\partial\Omega = \partial\Omega_N \cup \partial\Omega_F$. Condition (3) is a typical outflow boundary condition, while (4) is a typical inflow boundary condition.**

Note that in Sec. 3.4 there is a remark concerning the extension to some kind of Dirichlet conditions.

Let us state the assumptions required for Sec. 3.2. The condition on p in Assumption 1 is required for the compact embedding (5). The requirement that the stoichiometric coefficients are not in $(0,1)$ (Assumption 2) is used in the uniqueness proof (Theorem 3.2); see also Sec. 3.4. The Assumption 3 collects what is explicitly required for the estimates of Sec. 3.2, and finally we need the Assumption 4 on the solvability of the linear advection-diffusion problem. (Let us remark that Ass. 3 might be already included in Ass. 4 to some extent.)

Assumption 1. *Let $p > n+1$ hold. Let $\partial\Omega \subset \mathbb{R}^n$ be bounded, and piecewise smooth with nonzero interior angles in the sense of [11] p. 9.*

Assumption 2. *The columns of matrix S are linear independent, and $s_{ij}^f, s_{ij}^b \in \{0\} \cup [1,\infty)$ for all i, j.*

Assumption 3. *Let $u_0 \in L_+^\rho(\Omega)$ for a $\rho > p\bar{s}$, where $\bar{s} = \max\{\|S^b\|_1, \|S^f\|_1\}$ and where $\|M\|_1 = \max_j \sum_i |m_{ij}|$ is the matrix column norm. Let A be symmetric uniformly positive definite with entries $a_{ij} \in L^\infty(Q_T)$: There is $\underline{a} > 0$ with*

$$\underline{a}\,|\xi|_n^2 \leq \langle A(t,x)\,\xi, \xi\rangle_n$$

for all $\xi \in \mathbb{R}^n$, $(t,x) \in \overline{Q}_T$. Let $\theta \in C(0,T; L_+^\infty(\Omega))$ with $\theta \geq \theta_0 > 0$. Let $q \in L^\infty(Q_T)^n \cap L^2(0,T; H^1(\Omega))^n$ with div $q = -\partial_t\theta \in L^\infty(Q_T)$, $\langle q, \nu\rangle_n \in L^\infty([0,T] \times \partial\Omega)$. Let $k_j^f, k_j^b \in \mathbb{R}_+$, and $b \in L^\infty(0,T; L^\infty(\partial\Omega_F))^I$.

Assumption 4. *The initial data, the boundary conditions/data, the smoothness of $\partial\Omega$, and the coefficient functions of (2)-(4) are given in such a way that the linear scalar problem*

$$\partial_t(\theta u) + \mathcal{L}u = f,$$

with initial and boundary conditions from Problem 2.1, has a solution $u \in W_p^{2,1}(Q_T)$ for arbitrary $f \in L^p(Q_T)$, and the solution depends continuously on f.

Remark 2.1. (a) The Assumption 1 on p assures that the embedding $W_p^1(Q_T) \subset C(\overline{Q}_T)$, hence, the embedding

$$W_p^{2,1}(Q_T) \subset C(\overline{Q}_T), \tag{5}$$

*However, it is not essential to postulate $\langle \nu, q\rangle_n \geq 0$ on $\partial\Omega_N$ or $\langle \nu, q\rangle_n \leq 0$ on $\partial\Omega_F$.

is compact (e.g., [1]); as a consequence, u_i and products and even polynomial expressions in the u_i are in $C(\overline{Q}_T)$. Let us remark that the condition on p may be weakened to $p > \frac{n}{2}+1$ for smooth $\partial\Omega$ [18].
(b) One can find concrete statements on the required regularity of the data in Assumption 4 for example in [18] (Sec. 9.2.3) and [11] (p. 342 ff, the remark at the end of §9 on p. 351, and p. 621 ff).

For later use we state that obviously

$$\partial_t(\theta u_i^2) = \begin{cases} (\partial_t\theta)\, u_i^2 + \theta\, \partial_t u_i^2, \\ \partial_t(\theta u_i)\, u_i + \frac{\theta}{2}\, \partial_t u_i^2. \end{cases}$$

Substracting half of the first from the second equation and using (1) we get

$$\frac{1}{2}\, \partial_t(\theta u_i^2) = \partial_t(\theta u_i) u_i + \frac{u_i^2}{2}\, \mathrm{div}\; q. \tag{6}$$

For later use we further state that an estimate

$$\|u\|^2_{L^2(\partial\Omega)} \le c\, \|u\|_{H^1(\Omega)} \|u\|_{L^2(\Omega)} \tag{7}$$

holds for all $u \in H^1(\Omega)$ with constant depending only on Ω. This is, if $\int_{\partial\Omega} u\, do = 0$ and the Assumption 1 on $\partial\Omega$ holds, a special case of [11] Ch. II, (2.21). Estimate (7) carries over to non-meanvalue-free u easily ([10] p. 159).

Furthermore we state that for $u, v \in L^\infty(\Omega)$ and $s \ge 1$,

$$\big| |u(x)|^s - |v(x)|^s \big| \le s\, \max\{\|u\|^{s-1}_{L^\infty(\Omega)}, \|v\|^{s-1}_{L^\infty(\Omega)}\}\, \|u - v\|_{L^\infty(\Omega)} \tag{8}$$

a.e. holds. This follows from the application of the mean value theorem to $\xi \to \xi^s$ and the monotonic growth of $\xi \to \xi^{s-1}$ for $s \ge 1$.

2.2. Nonnegativity of solutions

Nonnegativity of solutions for nonnegative initial values is already investigated in [16] for classical solutions and isolating boundary conditions. Since these restrictions do not hold for our problem, we give a simple proof of nonnegativity, based on the energy method, inspired by [14]. Let us introduce the following problem with the modified rate function

Problem 2.2. *Find* $u \in W_p^{2,1}(Q_T)^I$ *such that*

$$\partial_t(\theta u) + \mathcal{L}u = \theta\, S\, R(u^+) \tag{9}$$

with the same initial and boundary condition as Problem 2.1. Here, u^+ *denotes the (componentwise) positive part of vector* u*:*

$$u_i^+ = \max\{u_i, 0\}, \quad u_i^- = \min\{u_i, 0\}, \quad u_i = u_i^+ + u_i^-$$

Note that thanks to (1) the PDE (9) may be expressed as

$$\theta\, \partial_t u_i - \mathrm{div}(A \nabla u_i) + \langle q, \nabla u_i \rangle_n = \theta\, \langle s_i, R(u^+) \rangle_J, \quad i = 1, ..., I. \tag{10}$$

Here s_i denotes the i-th row of matrix S.

Lemma 2.1. *Let Assumptions 1 and 3 hold, and let us assume that u is a solution of Problem 2.2. Then $u \geq 0$ holds. Hence, u is obviously a solution of Problem 2.1.*

Proof. For a $\tau \in (0,T)$ we test the i-th equation of (9) by u_i^- on Q_τ and apply partial integration for the diffusive term. We set $Q_i^- := \{(t,x) \in Q_\tau \,|\, u_i(t,x) < 0\}$, $\Omega_i^-(t) = \{x \in \Omega \,|\, u_i(t,x) < 0\}$, which are open subsets since $u_i \in C(\overline{Q}_T)$. Since u_i^- is equal to u_i on Q_i^- and is zero otherwise, we may restrict the integration domain from Q_τ to Q_i^- and replace u_i by u_i^- there. For the term $\partial_t(\theta u_i^-)u_i^-$, we apply (6) on Q_i^-. We obtain

$$\begin{aligned}
&\int_{\Omega_i^-(t)} \tfrac{\theta(\tau,x)}{2}(u_i^-)^2(\tau,x)\,dx + \int_0^\tau \int_{\Omega_i^-(t)} \langle A\nabla u_i^-, \nabla u_i^-\rangle_n\,dx\,dt \\
= &\int_0^\tau \int_{\Omega_i^-(t)} \Big(-\tfrac{(u_i^-)^2}{2}\,\mathrm{div}\,q - \langle q, \nabla u_i^-\rangle_n\,u_i^- \\
&+ \theta u_i^- \sum_{j=1}^J (s_{ij}^b - s_{ij}^f)(R_j^f(u^+) - R_j^b(u^+))\Big)\,dx\,dt \\
&+ \int_0^\tau \int_{\partial\Omega} \langle A\nabla u_i^-, \nu\rangle_n\,u_i^-\,do\,dt
\end{aligned} \tag{11}$$

Note that we have used the nonnegativity of $u_{0,i}$. Next we exploit the structure information that the exponents in $R^f(u^+)$, $R^b(u^+)$ are the same as the coefficients s_{ij}^f, s_{ij}^b, resp.: If $s_{ij}^b > 0$ then $R_j^b(u^+)$ contains a nontrivial factor $(u_i^+)^{s_{ij}^b}$, and since $u_i^+ u_i^- = 0$, $u_i^- R_j^b(u^+) = 0$ follows. Analogously, if $s_{ij}^f > 0$ then $R_j^f(u^+)$ contains a nontrivial factor $(u_i^+)^{s_{ij}^f}$, hence, $u_i^- R_j^f(u^+) = 0$. As a result, there are only the reactive terms $\theta u_i^- \sum_{j=1}^J s_{ij}^b R_j^f(u^+) + s_{ij}^f R_j^b(u^+) \leq 0$, since $u_i^- \leq 0$.

Exploiting the boundary conditions the boundary integral in (11) equals

$$\int_0^\tau \int_{\partial\Omega_F} b_i u_i^-\,do\,dt + \int_0^\tau \int_{\partial\Omega_F} (u_i^-)^2\,\langle q, \nu\rangle_n\,do\,dt. \tag{12}$$

Since $b_i \geq 0$, $u_i^- \leq 0$, the first integral is estimated by zero. The same can be done to the second integral, if the assumption of Footnote $*$ is made. Otherwise we can estimate it by a constant times $\|u_i^-\|^2_{L^2([0,T]\times\partial\Omega)}$. Hence, using (7) and Cauchy's inequality, (12) is estimated by a term

$$\epsilon \int_0^\tau \|\nabla u_i^-\|^2_{L^2(\Omega)^n}\,dx\,dt + C_\epsilon \int_0^\tau \|u_i^-\|^2_{L^2(\Omega)}\,dx\,dt; \tag{13}$$

the constant C_ϵ depends on $\epsilon > 0$ and the data. The two advective terms in (11) can also be estimated by a term of the shape (13). Next we set $E(\tau) = \int_{\Omega_i^-(t)} \frac{\theta(\tau,x)}{2} u_i^-(\tau,x)^2\,dx$ and use the positivity $\theta \geq \theta_0 > 0$ to obtain

$$\begin{aligned}
&E(\tau) + \int_0^\tau \int_{\Omega_i^-(t)} \langle A\nabla u_i^-, \nabla u_i^-\rangle_n\,dx\,dt \\
\leq\;& \epsilon \int_0^\tau \|\nabla u_i^-\|^2_{L^2(\Omega_i^-(t))^n}\,dt + C_\epsilon \int_0^\tau E(t)\,dt.
\end{aligned}$$

Choosing $\epsilon = \underline{a}$, for instance, Gronwall's lemma leads to $E(\tau) \leq 0$ from which $u_i \geq 0$ follows. $\square$

2.3. A Lyapunov function for the ODE case

It is well known that for the ODE case,

$$u'(t) = SR(u(t)), \quad u(0) > 0, \tag{14}$$

describing an isotropic, closed system, a Lyapunov function inspired by the Gibbs free energy can be used. We give the argumentation how to derive an a priori estimate for the ODE case here, since it will be applied in a similar, but more technical way to the PDE case in Sec. 3. Note that we skip the proof of strict positivity of solutions of (14). Let us define the functions

$$\begin{array}{ll} g_i : \overline{\mathbb{R}}_+ \longrightarrow \mathbb{R}, & g_i(\xi_i) = (\mu_i - 1 + \ln \xi_i)\, \xi_i + \exp(1 - \mu_i), \\ g : \overline{\mathbb{R}}_+^I \longrightarrow \mathbb{R}, & g(\xi) = \sum_{i=1}^{I} g_i(\xi_i). \end{array} \tag{15}$$

The constants μ_i, $i = 1, ..., I$, are defined as follows: Let $\mu \in \mathbb{R}^I$ be a solution of the linear system

$$S^T \mu = -\ln K \tag{16}$$

where $K \in \mathbb{R}^J$ is the vector of equilibrium constants $K_j = k_j^f / k_j^b$ related to the J reactions. Note that, due to Assumption 2, matrix S has maximal column rank J, i.e., the range of S^T is the whole $\mathbb{R}^J$. Hence, a solution μ of (16) exists. (In general, μ is not unique.) An important property of g_i, g is that

$$g_i'(\xi_i) = \mu_i + \ln \xi_i, \quad \frac{dg}{d\xi} = \mu + \ln \xi.$$

Note that g_i, g are also well defined for zero concentrations (but g_i', $dg/d\xi$ are not). A simple computation (computing the minimum of the two functions $\xi_i \mapsto g_i(\xi_i) - \xi_i$ and $\xi_i \mapsto g_i(\xi_i)$, $\overline{\mathbb{R}}_+ \to \mathbb{R}$), shows that

$$g_i(\xi_i) \geq \xi_i \quad \text{and} \quad g_i(\xi_i) \geq e^{-\mu_i}\,(e-1) > 0 \quad \text{for all } \xi_i \in \overline{\mathbb{R}}_+; \tag{17}$$

in fact, the additive constant $\exp(1-\mu_i)$ incorporated in the definition (15) of g_i was chosen in such a way that g_i dominates ξ_i. By (17); any bound for $g(\xi)$ immediately leads to a bound for ξ:

$$g(\xi) \geq g_i(\xi_i) \geq \xi_i \quad \forall \xi \in \overline{\mathbb{R}}_+^I, \quad i = 1, ..., I. \tag{18}$$

One can show easily that the mapping $t \longmapsto g(u(t))$, where $u(t)$ is a (local) solution of (14), is nonincreasing:

$$\begin{aligned} \frac{d}{dt}\, g(u(t)) &= \langle \nabla g(u(t)), u'(t) \rangle_I = \langle \mu + \ln u(t)\,,\, SR(u(t)) \rangle_I \\ &= \langle S^T \mu + S^T \ln u(t)\,,\, R(u(t)) \rangle_J \\ &= \langle -\ln K + S^T \ln u(t)\,,\, R(u(t)) \rangle_J \leq 0. \end{aligned} \tag{19}$$

The nonpositivity of (19) results from the fact that for each component $j = 1, ..., J$ of the inner product, the one factor is positive/zero/negative if and only if the other factor is negative/zero/positive: In fact, for $j = 1, ..., J$,

$$\begin{aligned} R_j(u) \lesseqqgtr 0 \quad &\Longleftrightarrow \quad R_j^f(u) \lesseqqgtr R_j^b(u) \\ &\Longleftrightarrow \quad \ln k_j^f + \sum_{i=1}^{I} s_{ij}^f \ln u_i \lesseqqgtr \ln k_j^b + \sum_{i=1}^{I} s_{ij}^b \ln u_i \\ &\Longleftrightarrow \quad 0 \lesseqqgtr -\ln K_j + \sum_{i=1}^{I} s_{ij} \ln u_i, \end{aligned} \tag{20}$$

which completes the proof of (19). The monotonicity of $t \mapsto g \circ u(t)$ (19) expresses the attempt of the system to reach chemical equilibrium.

Estimates (18) and (19) lead to the bound

$$0 \le u_i(t) \le g(u(t)) \le g(u(0)) = \text{const} \tag{21}$$

for every i and for all t for which the (local) solution u exists. Hence, a global solution of (14) exists (e.g., [7]).

3. The a priori estimate

3.1. Some auxiliary functions, and the basic ideas

A straight forward idea to generalize the derivation of an estimate of the solution from the ODE case of Sec. 2.3 to the PDE case Problem 2.2 seems to use the mapping $t \to \int_\Omega g(u(t,x))\,dx$, where u is a solution. However, with (18), this leads to an a priori estimate of a solution u and of $u \ln u$ with respect to the $L^\infty(0,T;L^1(\Omega))^I$ norm. Such an estimate is useful for problems with moderate nonlinear rate terms [13, 14], but it is not sufficient to bound the right-hand side of the PDE system (9). Instead, we will use the $L^r(\Omega)$ norm of $g \circ u$ to define the Lyapunov function, since this will provide an a priori estimate in $L^\infty(0,T;L^r(\Omega))$. For sufficiently large $r = r(p)$ (such as $r = p\bar{s}$, $\bar{s}$ from Ass. 3), this estimate allows to bound the polynomial right hand side of the PDE in $L^p(Q_T)$ and will, thanks to Assumption 4, lead to an a priori estimate of u in $W_p^{2,1}(Q_T)$. We define for $r \ge 1$

$$f_r : \overline{\mathbb{R}}_+^I \longrightarrow \mathbb{R}, \quad f_r(\xi) = [g(\xi)]^r.$$

From (17) we immediatly obtain the lower bounds

$$f_r(\xi) = g(\xi)^r \ge [g_i(\xi_i)]^r \ge \xi_i^r, \quad f_r(\xi) \ge c(r) > 0 \tag{22}$$

for all $\xi \in \overline{\mathbb{R}}_+^I$, $i = 1, ..., I$, $r \in \mathbb{N}$. We define the mapping†

$$F_r : L_+^\infty(\Omega)^I \longrightarrow \mathbb{R}, \quad F_r(u) = \|\theta^{1/r} g(u)\|_{L^r(\Omega)}^r = \int_\Omega \theta(x)\, f_r(u(x))\,dx. \tag{23}$$

†Note that we suppress any possible dependence of F_r on t, inherited by θ, in the notation.

Combining (23) and (22) we have the lower bounds

$$F_r(u) \geq \theta_0 \int_\Omega u_i^r\, dx, \quad F_r(u) \geq c(r) > 0 \tag{24}$$

for all $u \in L_+^\infty(\Omega)$. where the constant depends on r and the data θ_0, Ω, but not on u. Thus, in order to find $L^\infty(0,T;L^r(\Omega))$-bounds for solutions u, it is sufficient to estimate the value of the functional F_r along u.

We will frequently make use of the (classical) derivative of $f_r : \overline{\mathbb{R}}_+^I \longrightarrow \mathbb{R}$,

$$\partial f_r(\xi) : \mathbb{R}_+^I \longrightarrow \mathbb{R}^I,\ \partial f_r(\xi) = r\,[g(\xi)]^{r-1}\,\frac{dg}{d\xi} = r\, f_{r-1}(\xi)\,(\mu + \ln \xi), \tag{25}$$

$r \in \mathbb{N}$. Note the different behaviour of f_r and ∂f_r for ξ approaching the boundary of the positive cone: For $\xi \longrightarrow \xi_0 \in \partial\mathbb{R}_+^I$, f_r is bounded since $(\mu_i - 1 + \ln \xi_i)\xi_i \to 0$ for $\xi_i \to 0$, while $\partial f_r(\xi)$ is unbounded, since $\mu_i + \ln \xi_i$ is unbounded and $f_{r-1}(\xi) \not\to 0$. This has the following consequences: While $f_r(u) \in L^\infty(\Omega)$ is well defined for $u \in L_+^\infty(\Omega)^I$, $\partial f_r(u)$ may not be well defined. However, if we have the strict positivity $u \in L_\delta^\infty(\Omega) = \{u \in L^\infty(\Omega)\,|\, u \geq \delta\}$, $\delta > 0$, then $\partial f_r(u) \in L^\infty(\Omega)$ is well defined. In fact, the following facts obviously hold true. The mappings

$$\begin{aligned} &F_r : L_+^\infty(\Omega)^I \to \mathbb{R}, \\ &\partial f_r : L_\delta^\infty([t_1,t_2]\times\Omega)^I \to L^\infty([t_1,t_2]\times\Omega)^I \end{aligned} \tag{26}$$

are continuous. These are direct consequences of the continuity of $f_r : \overline{\mathbb{R}}_+^I \to \mathbb{R}$ and of $\partial f_r : [\delta,\infty)^T \to \mathbb{R}$.

Let us lay out the main idea how to obtain an a priori estimate. If a function $v : Q_T \to \mathbb{R}_+^I$ is chosen such that $F_r(v)$, v, $\partial f_r(v)$ are sufficiently smooth, in particular, if v is strictly positive in the sense that $v \geq \delta > 0$ on $\overline{Q}_T$, then an equation

$$\begin{aligned} & F_r(v(t_2)) - F_r(v(t_1)) \\ = & \int_\Omega \int_{t_1}^{t_2} \partial_t[\theta(t,x)\, f_r(v(t,x))]\, dx\, dt \\ = & \int_{t_1}^{t_2} \int_\Omega \left[\theta\, \langle \partial f_r(v), \partial_t v\rangle_I + \partial_t \theta\, f_r(v)\right] dx\, dt, \end{aligned} \tag{27}$$

expressing basically the fundamental theorem of calculus, obviously holds. Since we cannot be sure that these requirements hold for an arbitrary solution $u \in W_p^{2,1}(Q_T)$ of Problem 2.2, we construct $u_\delta(t,x) := u(t,x) + \delta$ and choose a smooth function $v = v_\delta$, e.g., $v_\delta \in C^\infty(\overline{Q}_T)$, being an approximation to u_δ in $W_p^{2,1}(Q_T)$. Note that due to the embedding (5) v_δ is also an approximation of u_δ in $C(\overline{Q}_T)$, thus, of the solution u itself. In particular, without loss of generality, $v_\delta \geq \delta/2$ can be assumed, i.e., all terms in (27) (with $v = v_\delta$) are well defined, in particular $\partial f_r(v_\delta)$, and the left hand side is an approximation to $F_r(u(t_2) - F_r(u(t_1))$ because of the continuity of F_r (26). The right hand side of (27) (with $v = v_\delta$) is an approximation of

$$\int_{t_1}^{t_2} \int_\Omega \left(\theta\ \langle \partial f_r(u_\delta), \partial_t u_\delta\rangle_I + \partial_t \theta\, f_r(u_\delta)\right) dx\, dt. \tag{28}$$

Since $\partial_t u_\delta = \partial_t u$, the PDE (10) can be applied to the first term of (28) where $\partial f_r(u_\delta)$ has the role of a test function. Exploiting $u_\delta \geq \delta$, one can check that $\partial f_r(u_\delta) \in L^2(0,T;H^1(\Omega))^{I\times n}$ holds.‡ The resulting terms are estimated in Lemma 3.1 by a term $h(\delta,u,r)$ with the property $h(\delta,u,r) \to 0$ for $\delta \to 0$ and fixed u, r, plus some boundary term. This result will be used to establish the limited-growth-property (29) for $t \mapsto F_r(u(t))$, and, thereby, an $L^\infty(0,T)$-estimate for $F_r(u)$ and, using (24), an $L^r(Q_T)$-estimate for u (Lemma 3.2), from which, thanks to Assumption 4, an $W_p^{2,1}(Q_T)$ estimate follows (Lemma 3.3) when taking $r = r(p)$ sufficiently large.

3.2. Derivation of the a priori estimate

Let us start by stating a central result of this section, expressing the monotonicity/limited growth of the functional F_r along solutions:

Theorem 3.1. *Let the Assumptions 1-3 hold and let $0 \leq t_1 < t_2 \leq T$ be given. Let $u \in W_p^{2,1}(Q_T)^I$ be a solution of Problem 2.2. Then the estimate*

$$F_r(u(t_2)) \leq e^{c\, r^2\, (t_2 - t_1)}\, F_r(u(t_1)) \tag{29}$$

holds for all $r \in \mathbb{N}$, $r \geq 2$, where the constant $c > 0$ depends only on the data, but not on u, r, t_1, t_2.

Remark 3.1. (a) Compared to the ODE case (19), we do not obtain monotonicity, i.e., $c = 0$ in (29). This is caused by 'chemical energy' which may enter the domain through its boundary. The proof of Lemma 3.1 reveals that (29) holds with $c=0$ if the isolation condition

$$\langle q, \nu\rangle_n = 0 \quad \text{on } \partial\Omega \times (0,T] \quad \text{and} \quad (b = 0 \text{ or } \partial\Omega_F = \emptyset) \tag{30}$$

is assumed. If only $\partial\Omega_F = \emptyset$ then (29) holds with exponent independent of r.
(b) The proofs of Theorem 3.1 and Lemma 3.1 also hold for $r=1$ if we set $f_{r-2} = f_{-1} = 0$ and if $\partial\Omega_F = \emptyset$.

In preparation for the proof of Theorem 3.1, we prove the following lemma.

Lemma 3.1. *Let the assumptions of the previous theorem hold. Let $\delta > 0$, $u_\delta := u + \delta$. Then the estimate*

$$\begin{aligned} &\int_{t_1}^{t_2}\int_\Omega \left[\langle \partial f_r(u_\delta), \theta \partial_t u_\delta\rangle_I \, dx\, dt + \partial_t\theta\, f_r(u_\delta)\right] dx\, dt \\ \leq\ & c\, r^2 \int_{t_1}^{t_2} F_r(u_\delta(t))\, dt + h(\delta, u, r), \end{aligned} \tag{31}$$

holds where $c > 0$ is a constant independent of δ, u, r and where $h(\delta,u,r) \longrightarrow 0$ for $\delta \longrightarrow 0$ and fixed u, r.

Proof. (i). Due to Lemma 2.1 $u_\delta \geq \delta$ holds. Hence, $\partial f_r(u_\delta) \in L^2(0,T;H^1(\Omega))^{I\times n}$. As a consequence, we can use $\partial f_r(u_\delta)$ as a test function in the weak formulation of

‡This is not true for $\partial f_r(u)$, which is one reason for us to introduce u_δ.

(10) and get by integration by parts

$$
\begin{aligned}
&\int_{t_1}^{t_2}\int_{\Omega} \theta\, \langle \partial f_r(u_\delta), \partial_t u_\delta \rangle_I \, dx\, dt \\
= &\int_{t_1}^{t_2}\int_{\Omega} \langle \partial f_r(u_\delta), \theta \partial_t u \rangle_I \, dx\, dt \\
= &\ \mathcal{I}_{reac} + \mathcal{I}_{diff} + \mathcal{I}_{adv} + \mathcal{I}_{bdry}
\end{aligned}
$$

with

$$
\begin{aligned}
\mathcal{I}_{reac} &= \int_{t_1}^{t_2}\int_{\Omega} \theta\, \langle \partial f_r(u_\delta), SR(u^+) \rangle_I \, dx\, dt \\
\mathcal{I}_{diff} &= -\sum_{i=1}^{I}\int_{t_1}^{t_2}\int_{\Omega} \langle A\nabla u_i, \nabla[\partial f_r(u_\delta)]_i \rangle_n \, dx\, dt \\
\mathcal{I}_{adv} &= \int_{t_1}^{t_2}\int_{\Omega} f_r(u_\delta)\, \mathrm{div}\, q\, dx\, dt \\
\mathcal{I}_{bdry} &= \int_{t_1}^{t_2}\int_{\partial\Omega} \left(\sum_{i=1}^{I} \langle A\nabla u_i, \nu \rangle_n [\partial f_r(u_\delta)]_i \right) - \langle q, \nu \rangle_n\, f_r(u_\delta)\, do\, dt
\end{aligned}
\tag{32}
$$

Note that to obtain the term $\mathcal{I}_{adv}$, the chain rule $\sum_{i=1}^{I}[\partial f_r(u_\delta)]_i \langle \nabla u_i, q \rangle_n = \langle \nabla f_r(u_\delta), q \rangle_n$ was applied to the advective term, and afterwards integration by parts was performed.

The second term on the left side of (31) is equal to $-\mathcal{I}_{adv}$. Hence it remains to prove that

$$
\mathcal{I}_{react} + \mathcal{I}_{diff} + I_{bdry} \le c \int_{t_1}^{t_2} F_r(u_\delta(t))\, dt + h(\delta, u, r).
$$

In (ii)-(iv) we will estimate the three terms.

(ii). For the reactive term $\mathcal{I}_{reac}$ we get with (25) and $u^+ = u$ (Lemma 2.1)

$$
\mathcal{I}_{reac} = \int_{t_1}^{t_2}\int_{\Omega} \theta r f_{r-1}(u_\delta)\, \langle \mu + \ln u_\delta\,,\, SR(u) \rangle_I \, dx\, dt.
$$

We split the inner product into a main part and a remainder,

$$
\begin{aligned}
\langle \mu + \ln u_\delta\,,\, SR(u) \rangle_I &= \langle \mu + \ln u_\delta\,,\, SR(u_\delta) \rangle_I \\
&\quad + \langle \mu + \ln u_\delta\,,\, SR(u) - SR(u_\delta) \rangle_I .
\end{aligned}
\tag{33}
$$

Following (19)-(20) with u replaced by u_δ, the main part of (33) is nonpositive, i.e.,

$$
\langle \mu + \ln u_\delta\,,\, SR(u_\delta) \rangle_I \le 0.
$$

Since $\theta r f_{r-1}(u_\delta) \geq 0$ we obtain

$$\mathcal{I}_{reac} \leq \int_{t_1}^{t_2} \int_\Omega \theta r f_{r-1}(u_\delta) \, \langle \mu + \ln u_\delta, SR(u) - SR(u_\delta) \rangle_I \, dx \, dt.$$

Expanding[§] the term $[SR(u) - SR(u_\delta)]_i$, we obtain a representation as a sum in which each summand contains a factor $u_k^s - u_{k,\delta}^s$, with $s \geq 1$. By using (8), we can estimate this difference by a term $|u_k - u_{k,\delta}| = \delta$ times a factor which depends on the L^∞-norm of u_k, for $\delta \in (0, \delta_0]$. After separation of the common factor δ the remaining terms (products of the u_k) are in $C^0(\overline{Q}_T)$ and bounded in $L^\infty(Q_T)$ for fixed u, and $\delta \to 0$. The factor $f_{r-1}(u_\delta)$ is also bounded in $L^\infty(Q_T)$ for fixed u and $\delta \to 0$. It remains to show that the product consisting of the factor δ and the factor $\mu + \ln u_\delta$ goes to zero in $L^1((t_1, t_2) \times \Omega)^I$ for $\delta \to 0$ and fixed u. For this, it is sufficient to show that $\delta \ln(x + \delta) \to 0$ for $\delta \to 0$ uniformly w.r.t. $x \in [0, \|u\|_{L^\infty(Q_T)^I}]$, which is obviously true. Hence,

$$\mathcal{I}_{reac} \leq h(\delta, u, r) \stackrel{(\delta \to 0)}{\longrightarrow} 0$$

for fixed solution u and fixed r.

(iii). The integrand of $\mathcal{I}_{diff}$ is transformed using first (25) and then the product rule:

$$\begin{aligned}
& - \sum_{i=1}^I \langle A \nabla u_i, \nabla [\partial f_r(u_\delta)] \rangle_n \\
= & - \sum_{i=1}^I \langle A \nabla u_i, r \nabla [f_{r-1}(u_\delta)(\mu_i + \ln u_{\delta,i})] \rangle_n \\
= & -r \sum_{i=1}^I (\mu_i + \ln u_{\delta,i}) \, \langle A \nabla u_i, \nabla f_{r-1}(u_\delta) \rangle_n && (34) \\
& -r f_{r-1}(u_\delta) \sum_{i=1}^I \langle A \nabla u_i, \nabla (\mu_i + \ln u_{\delta,i}) \rangle_n && (35)
\end{aligned}$$

Applying the chain rule to $\nabla f_{r-1}(u_\delta)$, the term (34) evaluates to

$$\begin{aligned}
& - r \, (r-1) \, f_{r-2}(u_\delta) \sum_{i=1}^I (\mu_i + \ln u_{\delta,i}) \, \langle A \nabla u_i, (Du)^T (\mu + \ln u_\delta) \rangle_n \\
= & - r \, (r-1) \, f_{r-2}(u_\delta) \, \Big\langle A \Big[\sum_{i=1}^I (\mu_i + \ln u_{\delta,i}) \, \nabla u_i \Big], \, (Du)^T (\mu + \ln u_\delta) \Big\rangle_n \qquad (36) \\
= & - r \, (r-1) \, f_{r-2}(u_\delta) \, \langle A \, (Du)^T \, (\mu + \ln u_\delta), (Du)^T \, (\mu + \ln u_\delta) \rangle_n \leq 0.
\end{aligned}$$

The term (35) evaluates to

$$- r \, f_{r-1}(u_\delta) \sum_{i=1}^I \sum_{j,k=1}^n \frac{a_{jk} \, \partial_k u_i \, \partial_j u_i}{u_{\delta,i}} = - r \, f_{r-1}(u_\delta) \sum_{i=1}^I \frac{1}{u_{\delta,i}} \, \langle A \nabla u_i, \nabla u_i \rangle_n \leq 0.$$

[§] in the sense $a_1 \cdot \ldots \cdot a_s - \bar{a}_1 \cdot \ldots \cdot \bar{a}_s = \sum_{l=1}^s a_1 \cdot \ldots \cdot a_{l-1} \cdot (a_l - \bar{a}_l) \cdot \bar{a}_{l+1} \cdot \ldots \cdot \bar{a}_s$

Hence, $\mathcal{I}_{diff} \leq 0$.
(iv). The rest of the proof is devoted to the estimation of the boundary integral. Exploiting the boundary conditions, the boundary term (32) reads

$$\begin{aligned}
\mathcal{I}_{bdry} &= \sum_{i=1}^{I} \int_{t_1}^{t_2} \int_{\partial\Omega_F} (\langle q,\nu\rangle_n u_i + b_i)[\partial f_r(u_\delta)]_i \, do\, dt - \int_{t_1}^{t_2} \int_{\partial\Omega} f_r(u_\delta)\, \langle q,\nu\rangle_n \, do\, dt \\
&= -\int_{t_1}^{t_2} \int_{\partial\Omega} f_r(u_\delta)\, \langle q,\nu\rangle_n \, do\, dt + \sum_{i=1}^{I} \int_{t_1}^{t_2} \int_{\partial\Omega_F} b_i\, r f_{r-1}(u_\delta)\, (\mu_i + \ln u_{i,\delta})\, do\, dt \\
&\quad + \sum_{i=1}^{I} \int_{t_1}^{t_2} \int_{\partial\Omega_F} r f_{r-1}(u_\delta)\, (\mu_i + \ln u_{i,\delta})\, u_i\, \langle q,\nu\rangle_n \, do\, dt. \qquad (37)
\end{aligned}$$

Since $\mu_i + \ln u_{i,\delta} \leq c u_{i,\delta} \leq c g_i(u_{i,\delta}) \leq c g(u_\delta)$, the inequality $f_{r-1}(u_\delta)\, (\mu_i + \ln u_{i,\delta}) \leq c\, f_{r-1}(u_\delta)\, g(u_\delta) = c\, f_r(u_\delta)$ holds. Hence, we can estimate the second term in (37) by

$$\sum_{i=1}^{I} \int_{t_1}^{t_2} \int_{\partial\Omega_F} b_i\, r f_{r-1}(u_\delta)\, (\mu_i + \ln u_{i,\delta})\, do\, dt \leq c\, r \int_{t_1}^{t_2} \int_{\partial\Omega_F} f_r(u_\delta)\, do\, dt$$

where the constant depends on the $L^\infty(Q_T)^I$-norm of b and on the μ_i, but can be chosen independently of $\delta \in (0, \delta_0], u, r$. Note that we used $b_i \geq 0$ for this, since the factor $\mu_i + \ln u_{i,\delta}$ has no sign.

In order to estimate the last term in (37), we state that

$$f_r(u_\delta) = f_{r-1}(u_\delta)\, g(u_\delta) = f_{r-1}(u_\delta) \left(\sum_{i=1}^{I} (\mu_i + \ln u_{i,\delta} - 1)(u_i + \delta) + e^{1-\mu_i} \right).$$

By reordering the terms we obtain

$$\begin{aligned}
& f_{r-1}(u_\delta) \sum_{i=1}^{I} (\mu_i + \ln u_{i,\delta}) u_i \\
= \;& f_r(u_\delta) + f_{r-1}(u_\delta) \left(\sum_{i=1}^{I} u_{i,\delta} - e^{1-\mu_i} \right) - \sum_{i=1}^{I} \delta\, (\mu_i + \ln u_{i,\delta}) f_{r-1}(u_\delta) \\
\leq \;& 2\, f_r(u_\delta) + h(\delta, u, r),
\end{aligned}$$

where we set $h(\delta, u, r) = \max_{(t,x)\in \overline{Q_T}} (-\sum_{i=1}^{I} \delta\, (\mu_i + \ln u_{i,\delta}) f_{r-1}(u_\delta))$ and where we used $f_{r-1}(u_\delta) \sum_{i=1}^{I} u_{\delta,i} \leq f_{r-1}(u_\delta) g(u_\delta) = f_r(u_\delta)$ in the last step. Note that $h(\delta, u, r) \longrightarrow 0$ for $\delta \to 0$ and u, r fixed. On the other hand,

$$f_{r-1}(u_\delta) \sum_{i=1}^{I} (\mu_i + \ln u_{i,\delta}) u_i \geq f_{r-1}(u_\delta) \sum_{i=1}^{I} (\mu_i + \ln u_i) u_i \geq -c\, f_{r-1}(u_\delta) \geq -c\, f_r(u_\delta)$$

holds, using (17) in the last step. Both estimates together yield

$$f_{r-1}(u_\delta)\left|\sum_{i=1}^{I}(\mu_i+\ln u_{i,\delta})u_i\right| \le c\, f_r(u_\delta)+h(\delta,u,r), \quad h(\delta,u,r) \overset{(\delta\to 0)}{\longrightarrow} 0$$

where the constant is independent of δ, u, r. Collecting the results and integrating, we estimate (37) by

$$\mathcal{I}_{bdry} \le c\, r \int_{t_1}^{t_2} \|f_r(u_\delta)\|_{L^1(\partial\Omega)} dt + h(u,\delta,r), \quad h(u,\delta,r) \overset{(\delta\to 0)}{\longrightarrow} 0. \tag{38}$$

In the following we demonstrate that this boundary integral of $f_r(u_\delta)$ can be absorbed by the term (36) in $\mathcal{I}_{diff}$ and by an $F_r(u_\delta)$-term. We start by noting that $f_r = (f_{r/2})^2$, i.e,

$$\|f_r(u_\delta)\|_{L^1(\partial\Omega)} = \|f_{r/2}(u_\delta)\|^2_{L^2(\partial\Omega)}, \quad \|f_r(u_\delta)\|_{L^1(\Omega)} = \|f_{r/2}(u_\delta)\|^2_{L^2(\Omega)},$$

and we apply (7) to $f_{r/2}(u_\delta)$. We obtain

$$\begin{aligned}
\|f_r(u_\delta)\|_{L^1(\partial\Omega)} &= \|f_{r/2}(u_\delta)\|^2_{L^2(\partial\Omega)} \\
&\le c\,(\,\|\nabla f_{r/2}(u_\delta)\|_{L^2(\Omega)^n}\,\|f_{r/2}(u_\delta)\|_{L^2(\Omega)} + \|f_{r/2}(u_\delta)\|^2_{L^2(\Omega)}) \\
&\le c\,(\epsilon\,\|\nabla f_{r/2}(u_\delta)\|^2_{L^2(\Omega)^n} + C_\epsilon\,\|f_{r/2}(u_\delta)\|^2_{L^2(\Omega)}) \\
&= c\left(\epsilon\int_\Omega \left|\nabla f_{r/2}(u_\delta)\right|_n^2 dx + C_\epsilon \int_\Omega f_r(u_\delta)\,dx\right)
\end{aligned} \tag{39}$$

where c only depends on the domain, and where $C_\epsilon = 1/(4\epsilon)$. The value of ϵ will be chosen later. An evaluation of the gradient yields

$$\begin{aligned}
\left|\nabla f_{r/2}(u_\delta)\right|_n^2 &= \left|\frac{r}{2}\, f_{\frac{r}{2}-1}(u_\delta)(Du_\delta)^T(\mu+\ln u_\delta)\right|_n^2 \\
&= \frac{r^2}{4}\, f_{r-2}(u_\delta)\,\left|(Du)^T(\mu+\ln u_\delta)\right|_n^2
\end{aligned} \tag{40}$$

Putting (38)-(40) together we get

$$\begin{aligned}
\mathcal{I}_{bdry} \;\le\; & h(\delta,u,r) + \frac{c\,C_\epsilon r}{\theta_0}\int_{t_1}^{t_2}\int_\Omega \theta\, f_r(u_\delta)\,dx\,dt \\
& +\epsilon\, c\,\frac{r^3}{4}\int_{t_1}^{t_2}\int_\Omega f_{r-2}(u_\delta)\,\left|(Du)^T(\mu+\ln u_\delta)\right|_n^2 dx\,dt
\end{aligned} \tag{41}$$

where the c only depend on q, μ, b, Ω. The first integral equals

$$\frac{c\,C_\epsilon r}{\theta_0}\int_{t_1}^{t_2} F_r(u_\delta)\,dt.$$

Now let us choose $\epsilon = \frac{2\,\underline{a}}{cr}$. Hence, $\epsilon \leq \frac{4\,\underline{a}\,(r-1)}{cr^2}$, since $r \geq 2$. Now $C_\epsilon r = \frac{r}{4\epsilon}$ only depends on $\underline{a}$, q, μ, b, Ω, and r, but not on δ, u. Due to this choice of ϵ, the second of the two integrals of (41) can be absorbed by $\mathcal{I}_{diff}$ (see (36)); i.e., (31) holds. □

Following the strategy outlined in the end of Sec. 3.1 we prove Theorem 3.1:

Proof of Theorem 3.1. Let $u \in W_p^{2,1}(Q_T)^I$ be a solution of Problem 2.2. Due to Lemma 2.1, we know that $u \geq 0$ on $\overline{Q}_T$. Let $\delta > 0$ be fixed and $u_\delta := u + \delta$. Let $v_\delta \in C^\infty(\overline{Q}_T)^I$ be an approximation of u_δ with respect to the $W_p^{2,1}(Q_T)$ norm. Then v_δ approximates u_δ and u in $L^\infty(Q_T)$, and we can assume that $v_\delta \geq \delta/2$.

The left hand side of (27), with $v = v_\delta$, is an approximation of $F_r(u(t_2)) - F_r(u(t_1))$. Exploiting the continuity of $\partial f_r : L^\infty_{\delta/2}(Q_T)^I \to L^\infty(Q_T)^I$ and of f_r, the right hand side of (27) (with $v = v_\delta$) is an approximation of (28). The term (28) is estimated as seen in (31). The right hand side of (31) converges to $c\int_{t_1}^{t_2} F_r(u(t))\,dt$ for $\delta \to 0$, exploiting again the continuity of F_r. Hence, for $\delta \to 0$ and $v_\delta \to u_\delta$, we get

$$F_r(u(t_2)) - F_r(u(t_1)) \leq cr^2 \int_{t_1}^{t_2} F_r(u(t))\,dt$$

for every solution u with c independent of u, r. Applying Gronwall's Lemma we obtain the desired result. □

From the theorem we derive the following a priori estimate in $L^\infty(0, T, L^r(\Omega))$ and so in $L^r(Q_T)$:

Lemma 3.2. *Let the Assumptions 1-3 hold. Then there are constants $c_1, c_2 > 0$ such that for arbitrary solutions $u \in W_p^{2,1}(Q_T)$ of Problem 2.2 and arbitrary $t \in [0, T]$ and $2 \leq r < \rho$) (ρ from Ass. 3),*

$$\|u(t)\|_{L^r(\Omega)^I} \leq c_1\, e^{c_2 r t}\, \|g(u_0)\|_{L^r(\Omega)} \tag{42}$$

holds.

Proof. By application of Theorem 3.1 we get

$$\begin{aligned} \int_\Omega u_i(t,x)^r\,dx &\leq \int_\Omega [g(u(t,x))]^r\,dx = \int_\Omega f_r(u(t,x))\,dx \leq \frac{1}{\theta_0}\,F_r(u(t)) \\ &\leq \frac{1}{\theta_0}\,e^{cr^2 t}\,F_r(u_0) = \frac{1}{\theta_0}\,e^{cr^2 t} \int_\Omega \theta(0,x)\,g(u_0(x))^r\,dx. \end{aligned} \tag{43}$$

The last integral exists since $g(u_0) \in L^r(\Omega)^I$ follows from $u_0 \in L^\rho(\Omega)^I$ for $r < \rho$. □

Remark 3.2. If $\partial\Omega_F = \emptyset$, then the exponent $c_2 rt$ in (42) can be replaced by $c_2 t/r$, which follows from the Remark 3.1 (a). Under this condition, and if we strengthen the assumption on u_0 (Ass. 3) to $u_0 \in L^\infty(\Omega)$, we may pass to the limit $r \to \infty$ to obtain an a priori estimate in $\|\cdot\|_{L^\infty(Q_T)}$, (cf. eg. [8], Sec. 10.E.1). However, we proceed directly to an a priori estimate in $W_p^{2,1}(Q_T)$ and apply a fixed point theorem, a technique that can also be generalized to more complicated reactive transport models such as couplings of PDEs and ODEs (see also [10, 13, 14]). Since we pick a fixed r, the behaviour of the bound (42) for $r \to \infty$ is not essential for what follows.

Lemma 3.3. *Let the Assumptions 1-4 hold. Then there is a constant $c > 0$, depending on the data of Problem 2.2 (possibly on T, p), but independent of u, such that for an arbitrary solution $u \in W_p^{2,1}(Q_T)^I$ of Problem 2.2*

$$\|u\|_{W_p^{2,1}(Q_T)^I} \leq c$$

holds.

Proof. Let $u \in W_p^{2,1}(Q_T)^I$ be a solution of Problem 2.2. The generalized Hölder inequality and application of Lemma 3.2 for $r = p\,\bar{s}$ (cf. Ass. 3) leads to the fact that the right hand side of our problem, $SR(u^+(t))$, meets an a priori bound in $L^p(Q_T)^I$:

$$\|SR(u^+)\|_{L^p(Q_T)^I} \leq c$$

From the assumption on the linear parabolic problem, Assumption 4, we obtain the existence of a constant c with $\|u\|_{W_p^{2,1}(Q_T)^I} \leq c$. □

3.3. Existence and uniqueness of the solution

With the a priori estimate of Lemma 3.3 we can derive the existence of a solution of Problem 2.2 by using a fixed point theorem, for example Schaefer's fixed point theorem (e.g., [3]). Let the assumptions 1-4 hold. The fixed point operator $\mathcal{Z}$ is defined by

$$\mathcal{Z} : W_p^{2,1}(Q_T)^I \longrightarrow W_p^{2,1}(Q_T)^I, \quad v \longmapsto u = \mathcal{Z}(v)$$

where u is the solution of the linear problem

$$\partial_t u + Lu = SR(v^+) \tag{44}$$

with the initial and boundary conditions of Problems 2.1,2.2.

Clearly, every fixed point of $\mathcal{Z}$ is a solution of Problem 2.2. Let us verify that $\mathcal{Z}$ is well defined. For $v \in W_p^{2,1}(Q_T)^I$ with $p > n+1$ the function v is contained in $C(\overline{Q}_T)^I$, as stated in (5). Hence, $v^+ \in C(\overline{Q}_T)^I$ and $SR(v^+) \in C(\overline{Q}_T)^I$. In particular, $SR(v^+) \in L^p(Q_T)^I$ holds. Due to the linear parabolic theory (Ass. 4), the existence of a unique solution u of problem (44) lying in $W_p^{2,1}(Q_T)^I$ follows.

The same steps show that the mapping $\mathcal{Z}$ is continuous and compact.

Theorem 3.2. *Let the Assumptions 1-4 hold. Then there is a unique solution of Problem 2.1.*

Proof. Let us apply for example Schaefer's fixed point theorem (see e.g. [3]). Since we know already the compactness of the mapping $\mathcal{Z}$, it remains to check that the set $\{u \in W_p^{2,1}(Q_T) \,|\, \exists \lambda \in [0,1] : \; u = \lambda \mathcal{Z}(u)\}$ is bounded. This is tantamount to prove an a priori bound for solutions of

$$\partial_t u + Lu = \lambda SR(v^+)$$

with initial and boundary values u_0, b replaced by λu_0, λb, $\lambda \in [0,1]$. It is obvious that the estimates of Sec. 3.2, derived for $\lambda = 1$, remain valid for $\lambda \in [0,1]$. Hence, we obtain the existence of a fixed point, i.e., of a solution of Problem 2.2. This solution is, due to Lemma 2.1, obviously also a solution of Problem 2.1. Let us show now that this solution of Problem 2.1 is unique.

Let $u^1, u^2 \in W_p^{2,1}(Q_T)^I$ be two solutions of Problem 2.1 and $\tilde{u} = u^1 - u^2$. We know that the u_i and all polynomial expressions in u are in $L^\infty(Q_T)$. We test the equations for u_i^1 and u_i^2 with $\tilde{u}_i$ on $[0,t] \times \Omega$ and take the difference. Similar as in the proof of Lemma 2.1 we obtain the energy estimate

$$\int_\Omega \frac{\theta}{2}\, \tilde{u}_i(\tau,x)^2\, dx + c \int_{Q_\tau} |\nabla \tilde{u}_i|_n^2\, dx\, dt \le \sum_{j=1}^J |s_{ij}| \int_{Q_\tau} \theta\, |R_j(u^1) - R_j(u^2)|\, |\tilde{u}_i|\, dx\, dt$$

where we have already exploited that $\tilde{u}(0,x) = 0$. It remains to consider the reactive term. Expanding all the terms of $R_j(u^1) - R_j(u^2)$ in the sense of Footnote §, every term in $R_j(u^1) - R_j(u^2)$ contains a factor of the structure $(u_l^1)^s - (u_l^2)^s$, which can be estimated, using (8), by a factor $|u_l^1 - u_l^2| = |\tilde{u}_l|$ times a constant depending on the L^∞-norms of u_l^1, u_l^2. So in the expansion of $R_j(u^1) - R_j(u^2)$, every term can be estimated by a constant $\Lambda_{li}(u^1,u^2)$ times $|\tilde{u}_l|$. Hence, the integrand is estimated by a sum of terms of the shape $\Lambda_{li} |\tilde{u}_l|\, |\tilde{u}_i|$. By Cauchy's inequality we get

$$\|\tilde{u}_i(\tau)\|_{L^2(\Omega)}^2 \le c \int_0^\tau \|\tilde{u}\|_{L^2(\Omega)^I}^2\, dt$$

where c depends on the data and on u^1, u^2. Summing up over $i = 1, ..., I$ and application of Gronwall's lemma yields $\|\tilde{u}(t)\|_{L^2(Q_\tau)^I}^2 \le 0$ for all $\tau \in [0,T]$. □

3.4. Extensions

The requirement that the stoichiometric coefficients are not in the interval $(0,1)$ (cf. Ass. 2) is only needed for the uniqueness proof and may be dropped if we are only interested in the existence. To see this, note that for all $s \in (0,1]$, $x, y \ge 0$, $|x^s - y^s| \le |x-y|^s$ holds, which can be used in the proof of Lemma 3.1, part (ii), to estimate $|u_k^s - u_{k,\delta}^s|$ by δ^s, and since $\delta^s \ln(x+\delta) \to 0$ for $\delta \to 0$, the rest of the proof remains valid.

Finally, let us mention that the extension of the problem of Sec. 2.1 to Dirichlet boundary conditions on a part $\partial\Omega_D \subset \partial\Omega$ of the boundary is simple, if the boundary value $u_D > 0$ is constant and coincides with an equilibrium point of the reactive system, i.e., $S^T \ln u_D = \ln K$ holds. Then we may choose $\mu = -\ln u_D$ (cf. (16)). Then the Ω_D-part of $\mathcal{I}_{bdry}$ (cf. (32)) can be treated as follows. The estimation of the advective part of the boundary integral, either by the data $q, \partial\Omega, u_D$, or as in the proof of Lemma 3.1, is obvious. The diffusive term in the Ω_D-part of $\mathcal{I}_{bdry}$ can be written as the integral over terms $\hat{h}_i(u_i)[\partial f_r(u_D+\delta)]_i = \hat{h}_i(u_i) r f_{r-1}(u_D + \delta)(\mu_i + \ln(u_{D,i}+\delta))$, and the factor $\mu_i + \ln(u_{D,i}+\delta) = \mu_i + \ln u_{D,i} + \ln(1+\delta/u_{D,i}) = \ln(1+\delta/u_{D,i})$ goes to zero for $\delta \to 0$, u fixed, i.e., it behaves like the term for the flux boundary condition, $h(\delta, u, r)$, in Lemma 3.1 and can be treated in the same way.

4. Conclusion

An application of the Lyapunov technique to a different hydrogeoscientific kinetic model, the three-species Monod model for biodegradation in porous media, can be found in [14]. Since the nonlinearities of the Monod model are moderate, the usage of $g(u)$ as a Lyapunov function, i.e., the availability of an $L^\infty(0,T;L^1(\Omega))$-estimate for $u\ln u$, is sufficient for that model to derive an a priori estimate. We modify this approach by using $f_r(u)$ to obtain an $L^\infty(0,T;L^r(\Omega))$-estimate.

In [15] an estimate $\partial_t g(u)+Lg(u)\le 0$ for $L=-\Delta$ is established for full high-order mass action kinetics, which allows the application of the maximum principle to show (together with suitable boundary conditions) that the maximum of $g(u)$ is attained at $t=0$, i.e., $g(u)$ and so u can be bounded using $g(u_0)$. This procedure seems less technical that the estimate of f_r, with $r>1$, in Sec. 3.2. However, the argumentation is based on the assumptions of strict positivity of solutions, on classical solutions, and homogeneous Neumann boundary conditions. We have applied the Lyapunov technique with $f_r(u)$ with relaxed assumptions and have seen that it is a viable alternative. In fact, in the model of Sec. 2-3 we may even start with constant $u_0\equiv 0$ and concentrations entering the domain through the boundary, with the maximum of $g(u)$ taken at some $t>0$, $x\in\partial\Omega$. Applications to extended models with additional terms in the PDEs or additional ODEs coupled to the PDEs ([13, 14], [10] Sec. 3.4) are possible.

A restriction both of the $f_r(u)$-method and of the method [15] for the moment seems that they exploit that the diffusion/dispersion operator is the same for all species u_i. The reason, for the $f_r(u)$-method is, that for $r>1$ the estimate of the diffusive term fails if the diffusion A is replaced by a species-dependent A_i. However, note that the presented method still gives an $L^\infty(0,T,L^1(\Omega))$ a priori bound for u and $u\ln u$ by using $r=1$ also for species-dependent diffusion, since the crucial term (36) is not present at all for $r=1$ (provided (30) holds). The question if the $f_r(u)$-method may be extended to species-dependent diffusion is under current investigation.

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