THE FAST-SORPTION AND FAST-SURFACE-REACTION LIMIT
OF A HETEROGENEOUS CATALYSIS MODEL

Dedicated to Michel Pierre on the occasion of his 70th anniversary

Björn Augner and Dieter Bothe*
Fachbereich Mathematik, Technische Universität Darmstadt
Alarich-Weiss-Straße 10
64287 Darmstadt, Germany

Abstract. Within this paper, we consider a heterogeneous catalysis system consisting of a bulk phase \( \Omega \) (chemical reactor) and an active surface \( \Sigma = \partial \Omega \) (catalytic surface), between which chemical substances are exchanged via adsorption (transport of mass from the bulk boundary layer adjacent to the surface, leading to surface-accumulation by a transformation into an adsorbed form) and desorption (the reverse process). Quite typically, as is the purpose of catalysis, chemical reactions on the surface occur several orders of magnitude faster than, say, chemical reactions within the bulk phase, and sorption processes are often quite fast as well. Starting from the non-dimensional version, different limit models, especially for fast surface chemistry and fast sorption at the surface, are considered. For a particular model problem, questions of local-in-time existence of strong and classical solutions and positivity of solutions are addressed.

1. Introduction.

1.1. Continuum thermodynamic modelling of reactive fluid mixtures. In this paper, the modelling and analysis of a prototypical chemical reactor with a catalytic surface are considered. Mathematically, the chemical reactor is described by a bounded domain \( \Omega \subseteq \mathbb{R}^3 \), in which chemical substances \( A_i, \ i = 1, \ldots, N \), may diffuse and react with each other. The evolution in time of these substances can be described on different scales of accuracy, depending on the particular interest one has in the model: These include, e.g., atomistic models, models derived from statistical physics, continuum thermodynamic, or effective (integral) models. Whereas a model on atomic level would include way to many mechanical variables and evolutionary equations, e.g., position, (linear) momentum, angular momentum etc. and the interaction with all the other molecules, the model of a perfectly stirred tank would neglect any spatial dependence of the variables describing the system. Here, we consider a continuum thermodynamic description of the reaction-diffusion system, denoting, by \( c_i \) the concentration of the \( i \)th component of the mixture, which depends on the time variable \( t \) and on the spatial position \( z \in \Omega \). The

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* Corresponding author: Dieter Bothe, bothe@mma.tu-darmstadt.de.
evolution of thermodynamic variables such as $c_i$ will be described by balance laws which together with thermodynamic closure relations give a set of partial differential equations, then. The fundamental balance law is the individual mass balance

$$\partial_t \rho_i + \text{div}(\rho_i \mathbf{v}_i) = R_i(\rho), \quad t \geq 0, \ z \in \Omega,$$

where $\rho_i = M_i c_i$ is the mass density of species $A_i$ with $M_i > 0$ its molar mass, $\rho_i \mathbf{v}_i$ is the individual (total) mass flux of species $A_i$ as the product of its mass density $\rho_i$ and the continuum mechanical velocity $\mathbf{v}_i$, and $R_i(\rho)$ the total reaction rate for species $A_i$, $i = 1, \ldots, N$. The latter two have to be modelled via appropriate closure relations and may, in general, depend on the full vector $\rho = (\rho_1, \ldots, \rho_N)^T$ of mass densities and its gradient $\nabla \rho$. For the chemical reactions, it is usually (on a non-relativistic level) assumed that they are mass-conserving, so that $\sum_{i=1}^N R_i(\rho) = 0$, leading to the continuity equation

$$\partial_t \rho + \text{div}(\rho \mathbf{v}) = 0, \quad t \geq 0, \ z \in \Omega$$

with the total mass density $\rho = \sum_{i=1}^N \rho_i$ and the total mass flux density $\rho \mathbf{v} = \sum_{i=1}^N \rho_i \mathbf{v}_i$ as the sum of the respective individual quantities. One defines the barycentric velocity of the fluid mixture as $\mathbf{v} = \frac{1}{\rho} \sum_{i=1}^N \rho_i \mathbf{v}_i$ (assuming $\rho > 0$, i.e., no local vacuum) and the individual mass fluxes decompose into $\rho_i \mathbf{v}_i = \rho_i (\mathbf{v} + \mathbf{u}_i) = \rho_i \mathbf{v} + \mathbf{J}_i$, where $\mathbf{u}_i$ denotes the velocity of species $A_i$ and $\mathbf{J}_i = \rho_i \mathbf{u}_i$ the diffusive flux relative to the motion of the barycentre. Note that then, by definition, $\sum_{i=1}^N \mathbf{J}_i = 0$. Implicitly, here, the barycentric velocity has been identified with the mass averaged velocity $\mathbf{v}^{\text{mass}}$, which was questioned rather recently, cf., e.g., [21]. Introducing the molar reaction rates $r_i = \frac{1}{M_i} R_i$, the balance equations for the molar concentrations, viz.

$$\partial_t c_i + \text{div}(c_i \mathbf{v}_i) = r_i(c), \quad t \geq 0, \ z \in \Omega,$$

follow directly from the individual mass balances. Similar to the barycentric variables, one may introduce the molar averaged velocity $\mathbf{v}^{\text{mol}} = \frac{1}{c} \sum_{i=1}^N c_i \mathbf{v}_i$, where $c = \sum_{i=1}^N c_i$ denotes the total concentration density of the fluid, and $\mathbf{u}_i^{\text{mol}} = \mathbf{v}_i - \mathbf{v}^{\text{mol}}$ (the velocity of species $A_i$ relative to the molar averaged velocity $\mathbf{v}^{\text{mol}}$), and $\mathbf{j}_i^{\text{mol}} = c_i \mathbf{u}_i^{\text{mol}}$ (the molar diffusive flux), so that the molar balance equations may be rephrased as

$$\partial_t c_i + \text{div}(c_i \mathbf{v}^{\text{mol}} + \mathbf{j}_i^{\text{mol}}) = r_i(c), \quad t \geq 0, \ z \in \Omega.$$

Let us note in passing that diffusive mass fluxes will be denoted by capital $\mathbf{J}_i$, whereas molar diffusive fluxes will be written as $\mathbf{j}_i$. Without superscript, diffusive fluxes are taken relative to the barycentric motion of the fluid, whereas a superscript like “mol” indicates that the diffusive flux is taken relative to the molar averaged velocity.

To get a mathematically well-posed problem, certain boundary conditions have to be set at the boundary $\partial \Omega$ of the chemical reactor. Typical boundary conditions considered in the mathematical literature are, e.g., Dirichlet boundary conditions, Neumann boundary conditions or Robin boundary conditions. Often one finds the special case of no flux $(c_i \mathbf{v} + \mathbf{j}_i) \cdot \mathbf{n} = 0$ boundary conditions (homogeneous Neumann boundary conditions), where $\mathbf{n}$ denotes the outer normal vector field on $\partial \Omega$. However, in the case of a bulk-surface reaction-diffusion-advection system as considered here, the boundary conditions on $c_i$ and/or $\mathbf{j}_i$ at $\partial \Omega$ are rather transmission conditions with a reaction-diffusion-advection system on the active surface $\Sigma \subseteq \partial \Omega$. Here, for simplicity, the case $\Sigma = \partial \Omega$ will be considered, but some amount of the
modelling and analysis carries over to the case of a boundary \( \partial \Omega \) which is disjointly decomposed into an active surface part \( \Sigma \subseteq \partial \Omega \) and, say, a no-flux boundary part \( \Sigma \setminus \partial \Omega \), assuming both to be relatively open to avoid problems due to so-called mixed boundary conditions. However, also additional technical difficulties may appear in a more general setup, e.g., if boundary parts of different type have non-disjoint boundary, or if the boundary is not impermeable, but allows for normal species flux. 

On the surface, the surface concentrations \( c_i^\Sigma \) as thermodynamic variables describe the molar concentration of species \( A_i^\Sigma \) (which is interpreted as an adsorbed version of species \( A_i \)) per area element, and it obeys the general reaction-diffusion-advection-adsorption balance equation

\[
\partial_t c_i^\Sigma + \text{div}_\Sigma (c_i^\Sigma \mathbf{v}^\Sigma_{\text{site}} + j_i^\Sigma_{\text{site}}) = r_i^\Sigma(c^\Sigma) + s_i^\Sigma(c^\Sigma, c^\Sigma), \quad t \geq 0, \ z \in \Sigma,
\]

where \(-\) similar to before \(-\) the individual mass flux is decomposed into a convective and a diffusive part via \( c_i \mathbf{v}^\Sigma_{\text{site}} = c_i^\Sigma \mathbf{v}^\Sigma_{\text{site}} + j_i^\Sigma_{\text{site}} \) with \( \mathbf{v}^\Sigma_{\text{site}} = \frac{1}{z} \sum_{i=0}^N c_i^\Sigma \mathbf{v}_i^\Sigma \) the site averaged velocity on the surface. Here and in the following, we restrict ourselves to the situation where there is a maximal capacity \( c_0^\Sigma \) (concentration of sites per area element on the solid surface), and each site can either be occupied by exactly one adsorbate or be free, i.e., unoccupied. In the latter case we think of the site being occupied by a species \( A_i^\Sigma \) (vacancies / free sites), where we set the vacancy concentration to

\[
c_0^\Sigma = c_0^\Sigma \sum_{i=1}^N c_i^\Sigma.
\]

One may think of \( \Sigma \) being covered by a condensed film of molecules, whereas \( \Omega \) is filled with a gas mixture. Then \( j_i^\text{site}(t, \cdot) = c_i \mathbf{u}_i^\text{site} = c_i (r_i^\Sigma - \mathbf{v}^\Sigma_{\text{site}}) \) denote the diffusive surface fluxes, \( r_i^\Sigma(c^\Sigma) \) the molar surface reaction rates and \( s_i^\Sigma(c^\Sigma, c^\Sigma) = j_i^\Sigma \cdot \mathbf{n} \) the normal flux through \( \Sigma \) has the meaning of a sorption rate. Here, by \( \text{div}_\Sigma \) we denote the surface divergence which may be equivalently defined by charts for any continuously differentiable extension of \( \mathbf{v}^\Sigma_{\text{mol}} : \Sigma \rightarrow \mathbb{R}^n \) to a neighbourhood of \( \Sigma \). Note that in this bulk-surface model, the molar surface concentrations \( c_i^\Sigma \) do not coincide with the restriction of the molar concentrations in the bulk phase to the surface, i.e., usually \( c_i^\Sigma \neq c_i | \Sigma \). For the sorption rates \( s_i^\Sigma(c^\Sigma, c^\Sigma) \) (defined as the normal fluxes), we look for suitable models for the sorption mechanisms at the surface so that, instead of the model

\[
\partial_t c_i + \text{div}(c_i \mathbf{v} + j_i) = r_i(c), \quad 1 \leq i \leq N, t \geq 0, \ z \in \Omega,
\]

\[
\partial_t c_i^\Sigma + \text{div}_\Sigma(c_i^\Sigma \mathbf{v}^\Sigma_{\text{site}} + j_i^\Sigma_{\text{site}}) = r_i^\Sigma(c^\Sigma) + (c_i \mathbf{v} + j_i) \cdot \mathbf{n}, \quad 1 \leq i \leq N, t \geq 0, \ z \in \Sigma,
\]

rather the following version will be considered throughout the paper:

\[
\partial_t c_i + \text{div}(c_i \mathbf{v} + j_i) = r_i(c), \quad 1 \leq i \leq N, t \geq 0, \ z \in \Omega,
\]

\[
\partial_t c_i^\Sigma + \text{div}_\Sigma(c_i^\Sigma \mathbf{v}^\Sigma_{\text{site}} + j_i^\Sigma_{\text{site}}) = r_i^\Sigma(c^\Sigma) + s_i^\Sigma(c^\Sigma, c^\Sigma), \quad 1 \leq i \leq N, t \geq 0, \ z \in \Sigma,
\]

\[
(c_i \mathbf{v} + j_i) \cdot \mathbf{n} = s_i^\Sigma(c^\Sigma, c^\Sigma), \quad 1 \leq i \leq N, t \geq 0, \ z \in \Sigma.
\]

At this point, the latter is just a rephrased version of the first formulation, but it has at least two advantages: First, the sorption rates \( s_i^\Sigma \) have a physical-chemical interpretation as describing transmission between the boundary layer of the bulk phase and the active surface as a kind of chemical reaction between species in the
boundary layer of the bulk phase and on the surface. Secondly, the transmission process constitutes a dissipative process, obeying to the entropy law of thermodynamics. On the other hand, writing \( s_i^\Sigma = s_i^\Sigma(c_{|\Sigma}^z, c^\Sigma) \) hints that we want to model these sorption rates by a model where the sorption rates depend on the concentrations \( c \) in the boundary layer and \( c^\Sigma \) on the surface, or, more precisely, on their respective chemical potentials. A schematic sketch of a reaction-diffusion-sorption system is provided by Figure 1. For a more complete thermodynamic modelling of heterogeneous catalysis, including linear momentum and internal energy balance, see [48] and the references given there.

1.2. On the convective part of mass-transport. The total mass density of a fluid evolves w.r.t. the continuity equation

\[
\partial_t \rho + \text{div}(\rho \mathbf{u}) = 0, \quad t \geq 0, \quad z \in \Omega.
\]

Thus, for a thermodynamically fully consistent model, there is a strong interplay between the barycentric velocity, the evolution of which depends on the total mass density \( \rho = \sum_i \rho_i \) of the fluid, and the individual mass balance, which again involves the barycentric velocity, so that the barycentric velocity influences, but also depends on the change of mass density due to diffusion and chemical reactions as well. In particular, a full model needs to include not only the solutes which are dissolved within a solvent, but the solvent itself as well. This makes such models highly complicated with delicate interaction between the several evolution mechanisms, and we will abstain from this most general setting. Instead, we consider only the evolution of the mass densities of the dissolved solutes \( A_i, \ i = 1, \ldots, N \). Consequently, the model cannot be expected to respect, e.g., conservation of linear momentum anymore, since any interaction between the solutes and the solvent is
neglected. Moreover, the barycentric velocity is only the barycentric velocity of
the solutes instead of the whole fluid mixture. Therefore, suitable models for the
barycentric velocity (of the solutes) are required. These may not be subject to mo-
momentum conservation, but only allow for some weakened form of thermodynamic
consistency. Possible approaches are the following:

(a) **Darcy’s law**: A common approximation used especially for porous media is
the Darcy law

\[ \mathbf{v} = -\alpha \nabla p \]

with the pressure \( p \) which by the Gibbs-Duhem relation is given by

\[ p = \sum_{i=1}^{N} c_i \mu_i - c_\psi \]

with \( \mu_i \) denoting the (molar) chemical potentials and \( \psi \) the (molar) free energy.
In the isothermal case, the gradient of the pressure is directly related to the
gradient of the chemical potentials via

\[ \nabla p = \sum_{i=1}^{N} c_i \nabla \mu_i. \]

This approach, as a means to eliminate the momentum equation in a reason-
able (for certain cases) way, has recently been employed in [32]. It leads to
the velocity model

\[ \mathbf{v} = -\alpha \sum_{i=1}^{N} c_i \nabla \mu_i. \]

(b) **Experimental observations**: As mentioned in [34], the molar averaged velocity
comes closest to the (weighted) averaged velocity which can be experimentally
measured. If one then restricts to systems at rest (in the sense of vanishing
molar averaged velocity), i.e., \( \mathbf{v}^{\text{mol}} \approx \mathbf{0} \), one may derive the barycentric ve-
locity from this as

\[ \mathbf{v} = -\sum_{i=1}^{N} \frac{1}{cM_i} \mathbf{J}_i^{\text{mol}} \]

where \( \mathbf{J}_i^{\text{mol}} \) denotes the mass flux relative to the molar averaged velocity of
the fluid, i.e., \( \rho_i \mathbf{v}_i = \rho_i \mathbf{v}_i^{\text{mol}} + \mathbf{J}_i^{\text{mol}} \).

(c) **Perturbation approach**: If the barycentric velocity \( \mathbf{v} \) and its divergence field
\( \text{div} \mathbf{v} \) are small in a certain sense,

\[ \text{div}(c_i \mathbf{v}) = \mathbf{v} \cdot \nabla c_i + (\text{div} \mathbf{v}) c_i \]

may be interpreted as a perturbative term with respect to the unperturbed
system for \( \mathbf{v} = 0 \). We then consider \( \mathbf{v} \) as an additional perturbation which then
may be brought to the right-hand side of the balance equation for the molar
concentrations \( c_i \). Therefore, in derivation and mathematical analysis on the
surface we restrict ourselves to the unperturbed fundamental case \( \mathbf{v} = 0 \).
Note, however, that by neglecting advective terms (\( \mathbf{v} = 0 \)) full thermodynamic
consistency cannot be expected anymore. Thus, we can and will only aim for
a reduced form of thermodynamic consistency in the sense as explained below.
Similarly, to have momentum conservation of the subsequent limit models, one would need to take the particles constituting the solid into account. Since we are looking for models of reasonable complexity, on the surface we do not consider the molar fluxes w.r.t. the barycentre, but rather focus on relative velocities w.r.t. the site averaged velocity of the surface fluid, so that in particular \( \sum_{i=0}^{N} j_{i}^{\Sigma, \text{site}} = 0 \), and the further modelling and analysis will be done only for the unperturbed case of vanishing site averaged surface velocity \( v^{\Sigma, \text{site}} = 0 \).

1.3. Reduced thermodynamic consistency. When considering the prototypical situation of vanishing barycentric velocity \( v \equiv 0 \) in the bulk and site averaged velocity \( v^{\Sigma, \text{site}} = 0 \) on the surface, the reduced model cannot be expected to satisfy conservation of (linear) momentum, especially if one thinks of the exchange of momentum due to sorption processes at the surface. Since the solvent \( A_{N+1} \) and the solid surface are not included in the model, this does not come as a surprise. However, one sensibly may ask which thermodynamic principles are satisfied yet, so that one may hopefully consider a subclass of models for the closure relations for diffusion, chemical reaction, adsorption and desorption, which, though not fully thermodynamically consistent, still satisfy some reduced form of thermodynamic consistency.

In this manuscript, we consider isothermal systems, for which the second law of thermodynamics (entropy law) implies a free energy dissipation principle, namely

**Principle 1.1** (Free energy minimisation). Every thermodynamically consistent system which is isothermal seeks to minimise its total free energy \( F \), i.e., formally

\[
\frac{dF}{dt} \leq 0.
\]

Since the surface \( \Sigma = \partial \Omega \) is assumed to be static, i.e., does not move or evolve in time, we may define the total free energy of the coupled bulk-surface system as

\[
F(t) = \int_{\Omega} (\rho \psi)(t, z) \, dz + \int_{\Sigma} (\rho^{\Sigma} \psi^{\Sigma})(t, z) \, d\sigma(z)
\]

\[
= \int_{\Omega} (c \psi^{\text{mol}})(t, z) \, dz + \int_{\Sigma} (c^{\Sigma} \psi^{\Sigma, \text{mol}})(t, z) \, d\sigma(z).
\]

Here, \( \psi \) and \( \psi^{\Sigma} \) denotes the specific free energy densities in the bulk and on the surface, resp., and \( \psi^{\text{mol}} \), resp. \( \psi^{\Sigma, \text{mol}} \), the molar free energy densities. The free energy densities will be modelled such that \( \rho \psi \) can be expressed as \( c \psi^{\text{mol}} = f(c) = f(c_1, \ldots, c_N) \) and \( c^{\Sigma} \psi^{\Sigma, \text{mol}} = f^{\Sigma}(c^{\Sigma}) = f^{\Sigma}(c_0^{\Sigma}, c_1^{\Sigma}, \ldots, c_N^{\Sigma}) \), i.e., for the surface free energy density, the vacancies are treated as an independent species, though, under the constraint \( \sum_{i=0}^{N} c_i^{\Sigma} = c_S^{\Sigma} \). (For deriving a model for the surface diffusion this is a convenient choice as it implies some symmetry properties of the Fick-Onsager coefficients; see the next subsection.) The molar chemical potentials \( \mu_i^{\text{mol}} \) in the bulk and \( \mu_i^{\Sigma, \text{mol}} \) on the surface are then given by

\[
\mu_i^{\text{mol}} = \frac{\partial f}{\partial c_i}(c), \quad i = 1, \ldots, N \quad \text{and} \quad \mu_i^{\Sigma, \text{mol}} = \frac{\partial f^{\Sigma}}{\partial c_i^{\Sigma}}(c^{\Sigma}), \quad i = 0, 1, \ldots, N.
\]

Inserting the evolution equations for \( c \) and \( c^{\Sigma} \), and using the model approximation \( \nu = 0 \) and \( v^{\Sigma, \text{site}} = 0 \), one may compute (using the divergence theorem in the bulk and on the surface as well as \( s_{i}^{0} = -\sum_{i=1}^{N} s_{i}^{0} \)) the change of total free energy...
(formally) as

\[
\frac{dF}{dt} = \frac{d}{dt} \left( \int_{\Omega} (c \psi_{\text{mol}}(t, z) \, dz + \int_{\Sigma} (c^i \psi_{\Sigma,\text{mol}}) \, d\sigma(z)) \right)
\]

\[
= \int_{\Omega} \sum_{i=1}^{N} (\mu_i r_i + j_i \cdot \nabla \mu_i)(t, z) \, dz + \int_{\Sigma} \sum_{i=0}^{N} \left( \mu_i^\Sigma r_i^\Sigma + j_i^{\Sigma,\text{site}} \cdot \nabla_{\Sigma} \mu_i^\Sigma(t, z) \right) \, d\sigma(z)
\]

\[
+ \int_{\Sigma} \sum_{i=1}^{N} (\mu_i^\Sigma - \mu_0^\Sigma - \mu_i) s_i^\Sigma \, d\sigma(z).
\]

Similar to the formulation of the entropy production rate for fully thermodynamically consistent models, cf. [16], the dissipative terms may be regrouped as follows:

\[
\frac{dF}{dt} = \int_{\Omega} \sum_{i=1}^{N} \mu_i r_i \, dz + \int_{\Omega} \sum_{i=1}^{N} j_i \cdot \nabla \mu_i \, dz + \int_{\Sigma} \sum_{i=0}^{N} \mu_i^\Sigma r_i^\Sigma \, d\sigma(z)
\]

\[
+ \int_{\Sigma} \sum_{i=0}^{N} j_i^{\Sigma,\text{site}} \cdot \nabla_{\Sigma} \mu_i^\Sigma \, d\sigma(z) + \int_{\Sigma} \sum_{i=1}^{N} (\mu_i^\Sigma - \mu_0^\Sigma - \mu_i) s_i^\Sigma \, d\sigma(z)
\]

\[- \int_{\Omega} (\zeta^{\text{chem}} + \zeta^{\text{diff}}) \, dz - \int_{\Sigma} (\zeta^{\Sigma,\text{chem}} + \zeta^{\Sigma,\text{diff}} + \zeta^{\Sigma,\text{sorp}}) \, d\sigma(z),
\]

where the change of free energy is due to the entropy production rates corresponding to the different physical and chemical processes, namely

\[
\zeta^{\text{chem}} = - \sum_{i=1}^{N} \mu_i r_i,
\]

\[
\zeta^{\text{diff}} = - \sum_{i=1}^{N} j_i \cdot \nabla \mu_i,
\]

\[
\zeta^{\Sigma,\text{chem}} = - \sum_{i=0}^{N} \mu_i^\Sigma r_i^\Sigma,
\]

\[
\zeta^{\Sigma,\text{diff}} = - \sum_{i=0}^{N} j_i^\Sigma \cdot \nabla_{\Sigma} \mu_i^\Sigma,
\]

\[
\zeta^{\Sigma,\text{sorp}} = - \sum_{i=1}^{N} (\mu_i^\Sigma - \mu_0^\Sigma - \mu_i) s_i^\Sigma.
\]

We restrict ourselves to particular subclasses of closure relations, namely such that

\( r = (r_i)_{i=1,...,N} = r(\mu), \ J = (j_i)_{i=1,...,N} = J(c, \nabla \mu), \ r^\Sigma = (r_i^\Sigma)_{i=0,...,N} = r^\Sigma(\mu^\Sigma) \)

and

\( s^\Sigma = (s_i^\Sigma)_{i=1,...,N} = s^\Sigma(\mu^\Sigma_{\text{eff}} - \mu), \ J^\Sigma = (j_i^\Sigma)_{i=0,...,N} = J(c^\Sigma, \nabla_{\Sigma} \mu^\Sigma), \)

i.e.,

(a) the chemical reaction rates \( r_i \) in the bulk are determined by the (vector of) chemical potentials \( \mu = (\mu_1, \ldots, \mu_N)^T \);

(b) analogously, the chemical reaction rates \( r_i^\Sigma \) on the surface are a function of the surface chemical potentials \( \mu^\Sigma = (\mu_0^\Sigma, \mu_1^\Sigma, \ldots, \mu_N^\Sigma)^T \);

(c) diffusive fluxes \( j_i \) in the bulk can be expressed in terms of the vector of concentrations \( c \) and the gradient of chemical potentials \( \nabla \mu = (\nabla \mu_1, \ldots, \nabla \mu_N)^T \);

(d) similarly, surface diffusive fluxes \( j_i^\Sigma,\text{site} \) depend on the vector of surface concentrations \( c^\Sigma \) and the surface gradient of the surface chemical potentials \( \nabla_{\Sigma} \mu^\Sigma = (\nabla_{\Sigma} \mu_0^\Sigma, \ldots, \nabla_{\Sigma} \mu_N^\Sigma)^T \).
(e) finally, the sorption rates $s_i^\Sigma$ are modelled as functions of the difference of chemical potentials $\mu_{\text{eff},i}^\Sigma = \mu_i^\Sigma - \mu_0^\Sigma$ with $\mu_{\text{eff},i}^\Sigma = \mu_i^\Sigma - \mu_0^\Sigma$. To ensure that there is dissipation of free energy (not necessarily strict) for this particular class, we model the closure relations such that the contribution to the change of free energy from every thermodynamic subprocess is non-negative, i.e., the terms $\zeta_{\text{diff}}, \zeta_{\text{chem}}, \zeta_{\Sigma,\text{diff}}, \zeta_{\Sigma,\text{chem}}$ and $\zeta_{\Sigma,\text{surf}}$ all become non-negative for every thermodynamically feasible process.

Remark 1.2. The factor $-1$ and the symbol $\zeta$ for the several contributions to the consumption of free energy hint at the corresponding contribution to the entropy production for the respective thermodynamic subprocesses. For more details, we refer to the manuscript [11].

In the next subsection, we restrict ourselves to specific models for these closure relations.

1.4. Models for bulk and surface diffusion, chemical reactions and sorption processes. Within this subsection, the underlying models for the diffusion processes in the bulk and on the surface, as well as for the chemical reactions and the sorption at the boundary are introduced. The time scale analysis will be based on these particular models, however, it should be clear how to extend the arguments to the case of other types of models for the diffusion and/or chemical reactions, in particular to other models for the chemical potentials in the bulk or on the surface. The motivation and derivation of certain limit models will be established via the special case of Fickian diffusion in the bulk and a (single-site) multi-component Langmuir model on the surface and Fick–Onsager surface diffusion. More precisely, in the bulk $N$ chemical substances $A_i$, $i = 1, \ldots, N$, are considered which are dissolved in a solvent $A_{N+1}$. The concentrations $c_i$ of the solutes $A_i$ are assumed to be much smaller than the concentration of the solvent $A_{N+1}$, i.e., $c_i \ll c_{N+1}$, and, moreover, it is assumed that the solutes merely interact with the solvent, and interactions between distinct solutes can be neglected. Standard Fickian diffusion $j \Sigma, \text{site} = -d_i \nabla c_i$, where typically $d_i > 0$ depends on the distribution of $c$, can neither constitute a thermodynamic consistent model for the diffusive fluxes nor is it consistent with the constraint $\sum_{i=1}^N J_i = 0$. Keep in mind that the convective flux $c_i \mathbf{v}$ is treated as a perturbation and the basic analysis here will be restricted to the fundamental case $\mathbf{v} = 0$. For dilute systems, however, it is still a reasonably good approximation to more general and thermodynamically consistent diffusion models such as Fick-Onsager diffusion or Maxwell–Stefan diffusion models; cf. the representation of the inversion of the Maxwell–Stefan relations in [36, Lemma 2.2]. In this simplified situation, $d_i > 0$ will be further assumed to be constant, so that the bulk reaction-diffusion system takes the form

$$\partial_t c_i - d_i \Delta c_i = r_i(c), \quad i = 1, \ldots, N, \quad t \geq 0, \quad z \in \Omega.$$ 

On the surface, however, low surface concentrations would be an unrealistic assumption, so that Fickian diffusion is ruled out, but a Fick-Onsager diffusion model (or, a Maxwell-Stefan type model) is employed instead. Hence, it is assumed that

$$J_i^{\Sigma, \text{site}} = -\sum_{i=0}^N d_i^{\Sigma} (c_{\Sigma}^\Sigma) \nabla c_{\Sigma}, \quad i = 0, 1, \ldots, N,
where the Fick-Onsager surface diffusion coefficients $d_{ij}^\Sigma = d_{ji}^\Sigma$ are symmetric in $i, j \in \{0, 1, \ldots, N\}$. Moreover, the $d_{ij}^\Sigma$ sum up to zero, i.e.,

$$
\sum_{j=0}^{N} d_{ij}^\Sigma (c^\Sigma) = 0, \quad i = 1, \ldots, N
$$

since $\sum_{i=0}^{N} J_i^\Sigma, \text{site} = 0$ to have consistency with the definition of the diffusive fluxes, i.e., $J_i^\Sigma, \text{site} = c^\Sigma_i (v_i^\Sigma - v_i^\Sigma, \text{site})$ for the site averaged velocity $v_i^\Sigma, \text{site}$. Moreover, analogously to our treatment of the bulk phase, vanishing molar averaged velocity $v_i^\Sigma, \text{site} = 0$ will be assumed throughout. Hence, the surface reaction-diffusion-sorption model takes the form

$$
\partial_t c_i^\Sigma - \text{div}_\Sigma \left( \sum_{j=0}^{N} d_{ij}^\Sigma (c^\Sigma) \nabla c_j^\Sigma \right) = r_i (c^\Sigma) + s_i (c|_{\Sigma}, c^\Sigma), \quad i = 0, 1, \ldots, N.
$$

It remains to model the rate of chemical reactions in the bulk ($r_i$) and on the surface ($r_i^\Sigma$) as well as the sorption rates ($s_i^\Sigma$).

**Remark 1.3.** Throughout, we set

$$
r_0^\Sigma (c^\Sigma) = - \sum_{i=1}^{N} r_i (c^\Sigma), \quad s_0^\Sigma (c|_{\Sigma}, c^\Sigma) = - \sum_{i=1}^{N} s_i^\Sigma (c|_{\Sigma}, c^\Sigma).
$$

Then the balance equation for the vacancy concentrations $c_0^\Sigma$ has the same form as the balance equations for the adsorbates $A_i^\Sigma, i = 1, \ldots, N$.

To find a suitable mathematical model for the bulk chemistry, one typically starts with a set of formal reaction equations

$$
\sum_{i=1}^{N} \alpha_i^a A_i = \sum_{i=1}^{N} \beta_i^a A_i, \quad a = 1, \ldots, m
$$

and uses the (molar) chemical potentials $\mu_i = \mu_i^0(T) + RT \ln x_i, i = 1, \ldots, N$, which fit well to the Fickian modelling of the bulk diffusion. Note that, here, $\mu_i^0(T)$ is temperature-dependent but independent of the vector of concentrations $c$. Moreover, $R$ is the universal gas constant, $T > 0$ the absolute temperature which is assumed to be constant here (isothermal case) and $c^* = (c_1^*, \ldots, c_N^*)^T \in (0, \infty)^N$ is some reference concentration (depending on the choice of $\mu_i^0(T)$).

**Remark 1.4** (Free energy and pressure in the bulk). The (molar) chemical potentials $\mu_i(T) = \mu_i^0(T) + RT \ln x_i$, where $x_i = c_i/c_i^*$, correspond to free energy density in the bulk of the form

$$
c_{\psi}^{\text{mol}} = -p_0 + \sum_{i=1}^{N} c_i \left[ \mu_i^0(T) + RT (\ln x_i - 1) \right].
$$

By the Gibbs-Duhem relation, the corresponding pressure is

$$
p = \sum_{i=1}^{N} c_i \mu_i - c_{\psi}^{\text{mol}} = p_0 + RT \sum_{i=1}^{N} c_i.
$$
By the second law of thermodynamics (entropy principle) or the above reduced principle of free-energy minimisation, for the thermodynamic subprocess of bulk chemistry one should have $\zeta^{\text{chem}} = \sum_i A_a R_a(c) \geq 0$ for the affinity

$$A_a = \sum_{i=1}^N \mu_i \mu^a_i = \sum_{i=1}^N (\mu^0_i + RT \ln \frac{c_i}{c_i^0})(\beta^a_i - \alpha^a_i)$$

of the $a$-th reaction. The reaction velocity of the $a$-th reaction is modelled as the difference of forward and backward reaction velocities $R_a = R^f_a - R^b_a$, so that we assume

$$(R^f_a - R^b_a) \sum_{i=1}^N (\mu^0_i + RT \ln \frac{c_i}{c_i^0})(\beta^a_i - \alpha^a_i) \geq 0.$$ 

In this paper, mass-action kinetics is used as a model for chemical reactions in the bulk. The latter may be derived as follows: For one, say the forward, direction of the reversible chemical reactions, a law of the type

$$R^f_a = k^f_a \prod_{i=1}^N c_i^{x_i} = \gamma \cdot k^f_a e^{\gamma^a}, \quad a = 1, \ldots, m$$

with some $k^f_a > 0$, typically depending on $T$ and $c$, is assumed (ansatz of reactive collisions). Then, to ensure positivity of the binary product $A_a R_a$, the backward reaction rate $R^b_a$ is determined by a logarithmic closure relation, viz.

$$\ln \frac{R^f_a}{R^b_a} = -\gamma^a \frac{1}{RT} A_a \quad \text{with} \quad \gamma^a > 0.$$ 

Note that, typically, the mixture is far away from chemical equilibrium, so that a linear closure is inappropriate and a logarithmic closure is used instead. In what follows, we let $\gamma^a = 1$ which is sufficient for our modelling purpose. This leads to the effective reaction velocity $R_a = k^f_a e^{\gamma^a} - k^b_a e^{\beta^a}$ with

$$\frac{k^b_a}{k^f_a} = (\mu^0)^{\nu^a} \quad \text{for} \quad \mu^0 = (\mu^0_1, \ldots, \mu^0_N)^T,$$

which (for the choice of chemical potentials $\mu_i = \mu^0_i + RT \ln \frac{c_i}{c_i^0}$) is exactly the standard mass-action kinetics law. Note that, w.l.o.g., one may assume $c^* i = 1$ (with physical dimension, though) after replacing $\mu^0_i$ by $\bar{\mu}^0_i = \mu^0_i - RT \ln c_i^0$. This convention will tacitly be used from now on.

On the surface, a realistic model for the chemical potentials should include the available space on the surface as well. One possibility to construct a model for the chemical potential is to assume that there is a maximal capacity $c^S_S > 0$ on the surface, as only limited space it available for the adsorbed species. This imposes the constraint $\sum_{i=1}^N c_i \leq c^S_S$ on the surface concentrations. Interpreting the free sites (or vacancies) as an additional species $A^V_S$ (see Figure 2) and denoting by $c^S_V := c^S_S - \sum_{i=1}^N c^S_i$ the vacancy concentrations, this constraint can be reformulated as

$$\sum_{i=0}^N c_i = c^V_S \quad \text{and} \quad c_i \geq 0, \quad i = 0, 1, \ldots, N. \quad \text{Introducing the occupancy numbers} \quad \theta_i := c^V_i / c^V_S, \quad i = 0, 1, \ldots, N, \text{this constraint may be equivalently expressed as} \quad \sum_{i=0}^N \theta_i = 1. \text{The surface free energy} \quad e^\Sigma \psi^\Sigma,\text{mol}$$
is modelled as that of an ideal mixture of the species $A_0^0$, $A_1^0$, ..., $A_N^0$, i.e., (Langmuir model)

$$c_{\Sigma\psi_0} = f_{\Sigma}(c_{\Sigma}) = -p_{\Sigma 0} + \sum_{i=0}^{N} c_i^0(\mu_i^{0,0}(T) + \ln \theta_i)$$

for some temperature-dependent parameters $\mu_i^{0,0}(T)$. One should keep in mind that $c_{\Sigma 0}^0 = c_{\Sigma}^0 - \sum_{i=1}^{N} c_i^0$ is not an independent variable, but nevertheless we assign a chemical potential $\mu_{\Sigma 0}^0$ to the vacancies $A_0^0$, so that

$$c_{\Sigma\psi,\text{mol}} = f_{\Sigma}(c_{\Sigma 0}, c_{\Sigma 1}, ..., c_{\Sigma N}).$$

The surface chemical potentials $\mu_i^\Sigma = \frac{\partial (c_{\Sigma\psi,\text{mol}})}{\partial c_i^\Sigma}$, $i = 0, 1, ..., N$, are then modelled as

$$\mu_i^\Sigma = \mu_i^{0,0}(T) + RT \ln \theta_i, \quad i = 0, 1, ..., N.$$

Moreover, by the Gibbs-Duhem relation, one may compute the surface pressure as

$$p_{\Sigma} = p_{\Sigma 0} + RT c_{\Sigma}.$$

Considerations similar to those for the bulk chemistry, transferred to the surface chemical reactions

$$\sum_{i=1}^{N} \alpha_i^{\Sigma,a} A_i^\Sigma \rightleftharpoons \sum_{i=1}^{N} \beta_i^{\Sigma,a} A_i^\Sigma, \quad a = 1, ..., m^\Sigma,$$

then lead to chemical reaction rates of the form

$$R_{\Sigma}^a = k_{a}^{\Sigma,f} \theta_{\Sigma}^{\Sigma,a} - k_{a}^{\Sigma, b} \theta_{\Sigma}^{\Sigma,a}, \quad a = 1, ..., m^\Sigma.$$
To do so, we interpret surface chemical reactions \( \sum_{i=1}^{N} \alpha_i^{\Sigma,a} A_i^{\Sigma} = \sum_{i=0}^{N} \beta_i^{\Sigma,a} A_i^{\Sigma} \) rather than chemical reactions of the type \( \sum_{i=0}^{N} \alpha_i^{\Sigma,a} A_i^{\Sigma} \), taking conservation of total sites into account and defining
\[
\alpha_0^{\Sigma,a} = \left\{ \begin{array}{ll}
\sum_{i=0}^{N} \nu_i^{\Sigma,a}, & \sum_{i=0}^{N} \nu_i^{\Sigma,a} \geq 0, \\
0, & \text{else}
\end{array} \right.
\]
\[
\beta_0^{\Sigma,a} = \left\{ \begin{array}{ll}
-\sum_{i=0}^{N} \nu_i^{\Sigma,a}, & \sum_{i=0}^{N} \nu_i^{\Sigma,a} \leq 0, \\
0, & \text{else}
\end{array} \right.
\]
so that \( \sum_{i=0}^{N} \nu_i^{\Sigma,a} = 0 \) for \( a = 1, \ldots, m^\Sigma \). Here, \( \theta = (\theta_0, \theta_{\text{red}})^T = (\theta_0, \ldots, \theta_N)^T, \alpha^{\Sigma,a} = (\alpha_0^{\Sigma,a}, \ldots, \alpha_N^{\Sigma,a})^T \) and \( \beta^{\Sigma,a} = (\beta_0^{\Sigma,a}, \ldots, \beta_N^{\Sigma,a})^T \). Moreover, the logarithmic closure gives the relations \( k_i^{\Sigma,b}/k_i^{\Sigma,f} = (\mu^{\Sigma,a})_{\theta_0^{\Sigma,a}} \). Finally, the sorption rates \( s_i^{\Sigma}(c) \) are modelled as reaction rates of chemical reactions of the form
\[
A_i = A_i^\Sigma, \quad \text{or}, \quad \text{taking site conservation into account}, \quad A_i + A_0^\Sigma = A_i^\Sigma.
\]
This leads to an effective reaction velocity of the form
\[
R_i^{\Sigma,\text{sorp}} = R_i^{\text{adv}} - R_i^{\text{de}} = k_i^{\text{ad}} c_i \theta_0 - k_i^{\text{de}} c_i^\Sigma, \quad i = 1, \ldots, N,
\]
where \( \ln \left( \frac{k_i^{\text{ad}}}{k_i^{\text{de}}} \right) = \mu_i^{\Sigma} - \mu_i^{\Sigma} - \mu_i^{\Sigma} \). To summarise, the bulk and surface chemistry, and the sorption rates are modelled as follows:
\[
r_i(c) = \sum_{a=1}^{m} \nu_i^{a}(k_i^f c^a - k_i^b c^b), \quad i = 0, 1, \ldots, N,
\]
\[
r_i^{\Sigma}(c) = \sum_{a=1}^{m^\Sigma} \nu_i^{\Sigma,a}(k_i^{\text{ad}} f c^{\Sigma,a} - k_i^{\text{de}} c^{\Sigma,b}) c_i^{\Sigma}, \quad i = 0, 1, \ldots, N,
\]
\[
s_i^{\Sigma}(c) = (k_i^{\text{ad}} c_i \theta_0 - k_i^{\text{de}} c_i^{\Sigma}) c_i^{\Sigma}, \quad i = 1, \ldots, N.
\]
In the case of vanishing convective fluxes, the condensed form of the full heterogeneous reaction-diffusion-sorption model reads as
\[
\partial_t c_i - d_i \Delta c_i = \sum_a \nu_i^{a}(k_i^f c^a - k_i^b c^b) \quad \text{in } (0, \infty) \times \Omega,
\]
\[
\partial_t c_i^{\Sigma} + \text{div} \, J_i^{\Sigma,\text{sorp}} = \sum_a \nu_i^{\Sigma,a}(k_i^{\text{ad}} f c^{\Sigma,a} - k_i^{\text{de}} c^{\Sigma,b}) c_i^{\Sigma} + (k_i^{\text{ad}} c_i \theta_0 - k_i^{\text{de}} c_i^{\Sigma}) c_i^{\Sigma} \quad \text{on } (0, \infty) \times \Sigma,
\]
\[
-d_i \nabla c_i \cdot \mathbf{n} = (k_i^{\text{ad}} c_i |\theta_0 - k_i^{\text{de}} c_i^{\Sigma}) c_i^{\Sigma} \quad \text{on } (0, \infty) \times \Sigma
\]
with \( J_i^{\Sigma,\text{site}} = -\sum_{j=0}^{N} d_i^{\Sigma}(c) \nabla c_j \), for \( i = 1, \ldots, N \).

**Remark 1.5.** One may as well consider \( c_i^{\Sigma} = c_i^{\Sigma} - \sum_{i=1}^{N} c_i^{\Sigma} \) and \( \theta_0 = 1 - \sum_{i=1}^{N} \theta_i \) as dependent functions of the \( c_i^{\Sigma} \)'s resp. \( \theta_i \), so that one might argue that the correct choice for the chemical potentials is
\[
\mu_i^{\Sigma} = \frac{\partial}{\partial c_i^{\Sigma}} \left( f(c_i^{\Sigma} - \sum_{j=1}^{N} c_j^{\Sigma}, c_i^{\Sigma}, \ldots, c_N^{\Sigma}) \right) = \mu_i^{\Sigma} - \mu_0^{\Sigma}.
\]
For this choice of the chemical potentials, however, the same reaction rate models result, as then \( A_i^{\Sigma} \) is not treated as an independent species. The advantage of our approach is the fact that the diffusive surface fluxes in the Fick–Onsager model satisfy certain symmetry conditions due to the choice that one models the diffusive surface fluxes relative to the site averaged molar flux. On the other hand, the equilibrium
condition at the surface would have the slightly simpler form $\mu_i|_{\Sigma} = \tilde{\mu}_i^\Sigma$ instead of the form $\mu_i|_{\Sigma} = \mu_i^\Sigma - \mu_0^\Sigma$ for $i = 1, \ldots, N$.

1.5. Dimensionless form of the bulk-surface reaction-diffusion-sorption model. Typically, the different thermodynamic processes, i.e., bulk and surface diffusion, bulk and surface chemical reactions as well as sorption processes, occur on different time scales. Indeed, quite often, especially for heterogeneous catalysis models, sorption processes and chemical reactions on the surface are considerably faster than all the other thermodynamic processes. From this perspective, it is natural to consider the fast sorption or fast surface chemistry limit models of the general reaction-diffusion-sorption model, so that the surface diffusion may (partly) be replaced by quasi-static relations between $c_i|_{\Sigma}$ and $c_i^\Sigma$, as will be seen below.

To derive a reduced limit model, one starts by establishing a dimensionless formulation of the general model, here the reaction-diffusion-sorption model with Fickian diffusion in the bulk and a Langmuir model on the surface. For this purpose, one introduces the following characteristic quantities:

- $t^R > 0$ with unit $[t^R] = s$, a characteristic time we can choose later on;
- $L_R, L_R^\Sigma > 0$ with $[L_R] = [L_R^\Sigma] = m$, characteristic lengths in the bulk and on the surface, referring to typical lengths over which differences in the concentration profile in the bulk or on the surface can be observed;
- $D_R, D_R^\Sigma > 0$ with $[D_R] = [D_R^\Sigma] = m^2/s$, characteristic diffusivities in the bulk and on the surface, referring to typical values of the diffusion coefficients $d_i$ in the bulk and $d_i^\Sigma(\Theta)$ on the surface;
- $c_R > 0$ with $[c_R] = \text{mol} \cdot \text{m}^{-3}$, a characteristic concentration in the bulk, referring to typical values of the molar concentrations $c_i$ in the bulk;
- on the surface, the maximal capacity $c^\Sigma_S$ (here assumed to be constant) with $[c^\Sigma_S] = \text{mol} \cdot \text{m}^{-2}$ naturally serves as area characteristic concentration;
- $k_{R,i}^{\text{ad}}, k_{R,i}^{\text{de}}> 0$ with $[k_{R,i}^{\text{ad}}] = m^3 \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$ and $[k_{R,i}^{\text{de}}] = \text{s}^{-1}$, characteristic adsorption and desorption parameters, referring to typical values of the reaction coefficients $k_{\text{ad}}^i$ and $k_{\text{de}}^i$, respectively;
- $k_{R,a,i}^f, k_{R,b}^f, k_{R,a}^{\Sigma,f}, k_{R,a}^{\Sigma,b}, k_{R,b}^{\Sigma,b}, k_{R,a}^{\Sigma,f}, k_{R,a}^{\Sigma,b}$, characteristic reaction constants for forward and backward chemical reactions in the bulk and on the surface with $[k_{R,a,f}^i] = (m^3 \cdot \text{mol}^{-1}) |\alpha^i| \cdot \text{s}^{-1}$, $[k_{R,a}^{\Sigma,f}] = (m^3 \cdot \text{mol}^{-1}) |\beta^\Sigma| \cdot \text{s}^{-1}$ and $[k_{R,a}^{\Sigma,f}] = [k_{R,a}^{\Sigma,b}] = m^2 \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$, respectively. Here, the standard notation $|\gamma| = \sum_{i=1}^N |\gamma_i|$ for vectors $\gamma = (\gamma_1, \ldots, \gamma_N)^T \in \mathbb{Z}^N$ is employed.

With these characteristic parameters at hand, one may define the following dimensionless variables and parameters:

- $t^* = t/t^R$;
- $z^* = z/L_R, \quad z^\Sigma^*, z = z/L_R^\Sigma$;
- $c_i^* = c_i/c_R$ and $c^* = (c_i^*)_{i=1}^N$;
- $\theta_i = c_i^\Sigma / c_i^\Sigma^*$ and $\Theta = (\theta_i)_{i=0}^N$;
- $d_i^* = d_i/D_R$ and $d_i^\Sigma^*, d_i^\Sigma = d_i^\Sigma / D_R^\Sigma$;
- $k_{i,a}^{\text{ad},*} = k_{i,a}^{\text{ad}} / k_{R,a}^{\text{ad}}$ and $k_{i,a}^{\text{de},*} = k_{i,a}^{\text{de}} / k_{R,a}^{\text{de}}$;
- $k_{a}^{f,*} = k_{a}^{f} / k_{R,a}^{f}$, $k_{a}^{b,*} = k_{a}^{b} / k_{R,a}^{b}$ and $k_{a}^{\Sigma,f,*} = k_{a}^{\Sigma,f} / k_{R,a}^{\Sigma,f}$, $k_{a}^{\Sigma,b,*} = k_{a}^{\Sigma,b} / k_{R,a}^{\Sigma,b}$. 
With a slight abuse of notation, one may also write $c^*_i(t^*, z^*) := c^*_i(t^* R, z^*)$ etc., and $\partial_t \cdot = \frac{1}{R} \partial_t$, $\div \cdot = \frac{1}{R} \div$, $\nabla \cdot = \frac{1}{R} \nabla$, $\div_\Sigma = \frac{1}{R} \div_\Sigma$, $\nabla_\Sigma = \frac{1}{R} \nabla_\Sigma$, and $\Delta_\Sigma = \frac{1}{(R \theta_\eta)^2} \Delta_\Sigma$, to get the following dimensionless version of the reaction-diffusion system with Fickian diffusion in the bulk and Fick-Onsager diffusion on the surface:

$$\frac{c_i}{R} \partial_t c_i - \frac{D c_i}{R} \Delta c_i = \sum_a \nu^a_i \left( k_{R, a}^c c_{R}^{\alpha | \alpha^a} k_{a}^{c \rho} (e^*)^{\alpha^a} - k_{R, a}^c c_{R}^{\beta | \beta^a} k_{a}^{c \rho} (e^*)^{\beta^a} \right) \quad \text{in } (0, \infty) \times \Omega,$$

$$\frac{1}{R} \partial_t \theta_i - \frac{D \theta_i}{R} \div_\Sigma \left( \sum_{j=0}^N d_{ij}^{\Sigma, \rho} \nabla_\Sigma \theta_j \right) = \sum_a \nu^{\Sigma, a}_i \left( k_{R, a}^{c \rho} k_{a}^{c \rho} (e^*)^{\Sigma^a} - k_{R, a}^{c \rho} k_{a}^{c \rho} (e^*)^{\Sigma^a} \right)$$

$$+ \left( k_{R, i}^{d \rho} c_{R}^{d \rho} c_{i}^{d \rho} \theta_i - k_{R, i}^{d \rho} c_{i}^{d \rho} \theta_i \right) \quad \text{on } (0, \infty) \times \Sigma,$$

$$\frac{c_R}{R} \partial_t c_R - \frac{D c_R}{R} \Delta c_R = k_{R, a}^{d} c_{R}^{d} c_{i}^{d} - k_{R, i}^{d} c_{i}^{d} \theta_i \quad \text{on } (0, \infty) \times \Sigma.$$
can be written in the following condensed dimensionless form.

The parameters

\[ \lambda_a^f = \frac{\tau_{\text{slow}}^{\text{react}}}{\tau_{\text{react}}^{\text{f},a}}, \quad \lambda_a^b = \frac{\tau_{\text{slow}}^{\text{react},\Sigma}}{\tau_{\text{react}}^{\text{f},a}}, \quad \lambda_a^{\Sigma,f} = \frac{\tau_{\text{slow}}^{\text{react},\Sigma}}{\tau_{\text{react}}^{\text{f},a}}, \quad \lambda_a^{\Sigma,b} = \frac{\tau_{\text{slow}}^{\text{react},\Sigma,b}}{\tau_{\text{react}}^{\text{f},a}}. \]

we may now introduce the following short-hand notation:

\[ r^*(c^*) = \sum_a \nu_i^a \left( \lambda_a^{f,a} (e^a)^{\alpha^a} - \lambda_a^{b,a} (e^a)^{\beta^a} \right), \]

\[ r^{\Sigma,*}(\theta) = \sum_a \nu_i^{\Sigma,a} \left( \lambda_a^{f,a} \theta^{\Sigma,a} - \lambda_a^{b,a} \Sigma^{\Sigma,b} \theta^{\Sigma,a} \right), \]

\[ s^{\Sigma,*}(c^*, \theta) = \lambda_i^{ad} c_i^* \theta - \lambda_i^{de} c_i^* \theta_i. \]

Remark 1.6. The parameters \( \lambda_a^f, \lambda_a^{\Sigma,f}, \lambda_a^{ad} \) may, in general, be very small, corresponding to chemical reactions in the bulk taking place on very dissimilar time scales. In that case an additional limit process is possible, which may lead, e.g., to some reversible reactions being replaced by an irreversible reaction, or to the negligence of slow reactions compared to faster reactions. Since the focus of this manuscript, however, lies on limit models for fast sorption and fast surface chemistry, we consider only the simpler case, where, e.g., \( \tau_{\text{slow}}^{\text{react},\Sigma} \ll \tau_{\text{slow}}^{\text{react}} \). I.e., we assume that even the slowest surface chemical reactions are faster than the fastest sorption processes.

With this notation at hand, the full bulk-surface reaction-diffusion-sorption model can be written in the following condensed dimensionless form.

\[ -\frac{1}{\tau^{\text{trans}}} d_i^* \partial_n c_i^* = \frac{1}{\tau^{\text{ad}}} k_i^{\text{ad},\Sigma} c_i^* \theta_0 - \frac{1}{\tau^{\text{de}}} k_i^{\text{de},\Sigma} \theta_i \quad \text{on } (0, \infty) \times \Sigma. \]

To prepare the dimensional analysis of the model, we denote by

\[ \tau_{\text{slow}}^{\text{react}} = \max \{ \tau_{\text{react}}^{f,a} : a = 1, \ldots, m \}, \]

\[ \tau_{\text{slow}}^{\text{react},\Sigma} = \max \{ \tau_{\text{react},\Sigma}^{f,a} : a = 1, \ldots, m \}, \]

the characteristic values for the slowest and fastest bulk reaction. Analogously, we define \( \tau_{\text{slow}}^{\Sigma} \geq \tau_{\text{fast}}^{\Sigma} > 0 \) and \( \tau_{\text{slow}}^{\text{sorp}} = \tau_{\text{slow}}^{\text{slow}} \geq \tau_{\text{slow}}^{\Sigma} > 0 \). Further, with

\[ \tau_{\text{slow}}^{\text{slow}} = \min \{ \tau_{\text{slow}}^{f,a} : a = 1, \ldots, m \}, \]

\[ \tau_{\text{slow}}^{\text{slow},\Sigma} = \min \{ \tau_{\text{slow}}^{\text{slow},\Sigma}^{f,a} : a = 1, \ldots, m \}, \]

we have

\[ \lambda_i^{f} = \frac{\tau_{\text{slow}}^{\text{slow}}}{\tau_{\text{slow}}^{\text{slow},\Sigma}}, \quad \lambda_i^{b} = \frac{\tau_{\text{slow}}^{\text{slow},\Sigma}}{\tau_{\text{slow}}^{\text{slow}}}, \quad \lambda_i^{\Sigma,f} = \frac{\tau_{\text{slow}}^{\Sigma}}{\tau_{\text{slow}}^{\Sigma,\Sigma}}, \quad \lambda_i^{\Sigma,b} = \frac{\tau_{\text{slow}}^{\Sigma,\Sigma}}{\tau_{\text{slow}}^{\Sigma}}, \]

\[ \lambda_i^{ad} = \frac{\tau_{\text{slow}}^{\Sigma}}{\tau_{\text{slow}}^{\Sigma}}, \quad \lambda_i^{de} = \frac{\tau_{\text{slow}}^{\Sigma}}{\tau_{\text{slow}}^{\Sigma}} \in [1, \infty). \]

2. Limit models. Within this section, several limit models, each of them corresponding to different ordering of the time scales \( \tau^{\text{diff},\Sigma}, \tau^{\text{react},\Sigma}, \tau^{\text{sorp}} \) and \( \tau^{\text{trans}} \) are motivated and derived. These constitute the most relevant cases for the dynamics on the surface and the transmission condition between bulk and surface. First, the
cases with only one fast thermodynamic process, corresponding to one of the time scale parameters being very small compared to the others, are investigated. Thereafter, cases of two or three very fast processes are considered as well, possibly with a structural relation between some of the fast processes, e.g., one of them being ultra-fast, i.e., even being very fast compared to other fast processes.

2.1. **One-parameter limits.** Starting with the case of exactly one fast physical or chemical process, (at least mathematically) the following four limit cases can be distinguished:

(a) fast surface chemistry, characterised by the condition
\[ \tau_{\text{slow}}^{\text{react, } \Sigma} \ll \tau_{\text{diff}, \Sigma}^{\text{diff}}, \tau_{\text{sorp}, \Sigma}^{\text{sorp}}, \tau_{\text{fast}}^{\text{fast}}; \]

(b) fast sorption processes, characterised by the condition
\[ \tau_{\text{slow}}^{\text{sorp}} \ll \tau_{\text{diff}, \Sigma}^{\text{diff}}, \tau_{\text{react, } \Sigma}^{\text{react}}, \tau_{\text{fast}}^{\text{fast}}; \]

(c) the fast surface diffusion case, characterised by the condition
\[ \tau_{\text{slow}}^{\text{diff, } \Sigma} \ll \tau_{\text{react, } \Sigma}^{\text{react}}, \tau_{\text{sorp}, \Sigma}^{\text{sorp}}, \tau_{\text{fast}}^{\text{fast}}; \]

(d) the case of fast transmission between surface and bulk, characterised by the condition
\[ \tau_{\text{trans}}^{\text{trans}} \ll \tau_{\text{diff, } \Sigma}^{\text{diff}}, \tau_{\text{react, } \Sigma}^{\text{react}}, \tau_{\text{sorp}, \Sigma}^{\text{sorp}}, \tau_{\text{fast}}^{\text{fast}}. \]

We will comment on the resulting reduced models and their physical significance in the following paragraphs.

2.1.1. **Fast surface chemistry.** First, assume that
\[ \tau_{\text{slow}}^{\text{react, } \Sigma} \ll \tau_{\text{diff, } \Sigma}^{\text{diff, } \Sigma}, \tau_{\text{slow}}^{\text{sorp, } \Sigma}, \tau_{\text{fast}}^{\text{fast}}. \]

This is quite a typical case for heterogeneous catalysts and means that, on the surface, the chemical reactions take place much faster than all other physical-chemical processes, in particular bulk and surface diffusion, bulk chemistry and sorption at the surface. From a chemical engineering point of view this often is the most desirable case.

**Remark 2.1.** It is possible to consider only some of the chemical reactions on the surface as being fast, leading to fewer (nonlinear) constraints below and additional slow or moderately fast surface reaction terms in the dynamics on \( \text{span}\{e^k\} \) as defined below. In this case, in the fast reaction limit, only some of the chemical reactions would be assumed to be infinitely fast whereas other reactions take place on the same time scale as the remaining physical and chemical mechanisms.

As the time scales differ, on which the different physical and chemical processes take place, we first consider the dynamics on a fine time scale, i.e., we choose \( \tau^R = \tau^R_{\text{fine}} = \tau^{\text{react, } \Sigma} \) as the time we want to observe the time evolution of the system. Then, multiplying the evolutionary equation on the surface (2) by \( \tau^R = \tau^{\text{react, } \Sigma} \) and then letting formally \( \tau^{\text{react, } \Sigma}, \tau_{\text{sorp, } \Sigma}^{\text{sorp}} \to 0 \), we obtain the system of ordinary differential equations
\[
\begin{align*}
\partial_t \theta^\text{fine} &= \tau^{\Sigma, \star}(\theta^\text{fine}) & \text{on } \Sigma, t \geq t_0^*, \\
\theta^\text{fine}((0, \cdot)) &= \theta^{\text{fine}, 0} & \text{on } \Sigma.
\end{align*}
\]
Assumption 2.2 (Detailed-balanced equilibria). Throughout this manuscript, we assume that all equilibria are detailed-balanced, i.e.,
\[ \nu_{\Sigma,1}, \ldots, \nu_{\Sigma,m} \] are linearly independent.

(As by definition \( \nu_{\Sigma,a} = -\sum_{i=1}^{N} \nu_{i,a} \), this condition is equivalent to the statement that \( \nu_{\Sigma,1}, \ldots, \nu_{\Sigma,m} \) with \( \nu_{\Sigma,a} := (\nu_{\Sigma,a})_{i=1,\ldots,N} \in \mathbb{R}^N \) are linearly independent.)

For \( \{ \nu_{\Sigma,a} : a \} \subseteq \mathbb{R}^N \) one then finds an (orthonormal) basis \( \{ e_k : k = 1, \ldots, n^\Sigma \} \subseteq \mathbb{R}^N \) (with \( n^\Sigma = N - m^\Sigma \)). Under the standing assumption that the surface chemical reactions only have detailed-balanced equilibria, we know the asymptotic long-time behaviour of this system of ODEs, namely
\[ \theta_{\text{fine}}(t^*,z^*) \xrightarrow{t \to \infty} \theta_{\text{eq}}(\theta_{\text{fine},0}(z^*)) \] at exponential rate,
where \( \theta_{\text{fine}} = \theta_{\text{eq}}(\theta) \in \mathbb{R}^N \) is the (unique) equilibrium state \( r_{\Sigma,*}(\theta_{\text{fine}}) = 0 \) respecting conservation of the conserved quantities \( \theta_{\text{eq}} \cdot e_k = \theta \cdot e_k \) for \( \{ e_1, \ldots, e_{n^\Sigma} \} \) forming a basis of the orthogonal complement to \( \{ \nu_{\Sigma,a} : a = 1, \ldots, m^\Sigma \} \). As the surface chemical reactions are very fast compared to surface diffusion and transmission, when switching to the coarser time scale \( \tau^R = \min\{ \tau^\text{diff.} \Sigma, \tau^\text{sorp} \} \) the dynamics, thus, may be well approximated by the quasi-steady relation
\[ r_{\Sigma,*}(\theta) = 0, \quad t^* \geq 0 \]
and the ‘remaining’ dynamics for the conserved quantities
\[ \frac{1}{\tau^R} \frac{\partial}{\partial \tau} e_k + \frac{1}{\tau^\text{diff.} \Sigma} \text{div}_{\Sigma} \left( D_{\Sigma,*}(\theta) \nabla_{\Sigma}^\theta \right) e_k = \frac{1}{\tau^\text{sorp}} s_{\Sigma,*}(c^*, \theta) \cdot e_k, \quad k = 1, \ldots, N-m, \]
where \( D_{\Sigma,*} = [d_{ij}^\Sigma,*]_{i,j} \in \mathbb{R}^{(1+N) \times (1+N)} \). Note that the quasi-steady nonlinear relation
\[ r_{\Sigma,*}(\theta) = 0 \]
is equivalent to
\[ r_{\text{red,*}}(\theta) = (r^\Sigma_{*,a}(\theta))_{i=1,\ldots,N} = 0 \]
due to the definition \( r^\Sigma_{*,a}(\theta) = -\sum_{i=1}^{N} r_{i,a,*}(\theta) \).

Remark 2.3. The condition \( r_{\Sigma,*}(\theta) = 0 \) can be interpreted as follows.

(a) First, consider the case \( m^\Sigma = 1 \), i.e., only one type of chemical reaction
\[ \sum_{i=0}^{N} \alpha_i^\Sigma A_i = \sum_{i=0}^{N} \beta_i^\Sigma A_i \] takes place on the surface. From the modelling of the chemical reaction rates one has
\[ R_{\Sigma,f}^{\Sigma,b} = -\exp \left( \frac{1}{RT} A_{\Sigma}^a \right) \]
and, provided none of the involved species vanish, \( R_{\Sigma} = R_{\Sigma,f} - R_{\Sigma,b} = 0 \) if and only if the affinity vanishes: \( A_{\Sigma}^a = \sum_{i=0}^{N} \mu_i^\Sigma v_i^\Sigma = 0 \).

(b) In case of \( m^\Sigma \geq 2 \) types of chemical reactions
\[ \sum_{i=0}^{N} \alpha_i^\Sigma A_i = \sum_{i=0}^{N} \beta_i^\Sigma A_i, \]
a = 1, \ldots, m, the condition \( r_{\Sigma,*}(\theta) = 0 \) is, in general, not equivalent to the condition \( A_{a}^\Sigma = 0 \) for \( a = 1, \ldots, m^\Sigma \). Equivalence of \( r_{\Sigma,*}(\theta) = 0 \) to the condition \( A_{a}^\Sigma = 0 \) for \( a = 1, \ldots, m^\Sigma \), holds true if and only if the stoichiometric vectors \( v_{\Sigma,a} \), a = 1, \ldots, \( m^\Sigma \), are linearly independent. More precisely, \( r_{\Sigma,*}(\theta) = 0 \) holds true if and only if \( R_{\Sigma}^{\Sigma,a}(\theta) = R_{\Sigma,a}^{\Sigma,f}(\theta) - R_{\Sigma,a}^{\Sigma,b}(\theta) = w_a \) for some vector \( w \in \ker \left( \left[ \nu_{\Sigma,1}, \ldots, \nu_{\Sigma,m} \right]^T \right) \subseteq \mathbb{R}^{m^\Sigma} \). Chemical equilibria for which \( w \neq 0 \) is allowed are called complex-balanced equilibria, in contrast to
the detailed-balanced equilibria with $w = 0$ (i.e., $A_a = 0$, $a = 1, . . . , m^\Sigma$). For the discussion of chemical reaction networks with complex-balanced equilibria, we refer, e.g., to [31] and related works.

(c) In any case, $r^\Sigma_{\Sigma^*}(\theta) \in \text{span}\{\mathbf{v}^{\Sigma,a} : a = 1, . . . , m^\Sigma\}$ and, hence, the static condition may replace the dynamic equation (2) only on $\text{span}\{\mathbf{v}^{\Sigma,a} : a = 1, . . . , m^\Sigma\}$, while on $\{\mathbf{v}^{\Sigma,a} : a = 1, . . . , m^\Sigma\}^\perp$ a dynamic condition still remains in the fast surface chemistry limit.

The resulting reduced model is given by a coupled bulk-surface reaction-diffusion-sorption-system with a nonlinear constraint on the surface occupancy numbers $\theta$:

\[
\frac{1}{\tau_R} \partial_t c^* - \frac{1}{\tau_{\text{diff}}} D^* \Delta c^* = \frac{1}{\tau_{\text{react}}} r^i_{\text{react}}(c^*), \quad t \geq 0, \, z \in \Sigma,
\]

\[
\frac{1}{\tau_R} e^k \cdot \partial_z, \theta_{\text{red}} - e^k \cdot \text{div}_\Sigma(D^* \nabla_{\Sigma}^* \theta) = \frac{1}{\tau_{\text{sorp}}} e^k \cdot s^{\Sigma,*}(c^*, \theta), \quad t \geq 0, \, z \in \Sigma,
\]

\[
-\frac{1}{\tau_{\text{trans}}} D^* \partial_n c^* = \frac{1}{\tau_{\text{sorp}}} s^{\Sigma,*}(c^*, \theta), \quad t \geq 0, \, z \in \Sigma,
\]

\[
r^{\Sigma,*}(\theta) = 0, \quad t \geq 0, \, z \in \Sigma,
\]

using the notation $D^* = \text{diag}(d^i_{\text{ext}})_{i \in \mathbb{N}^N}$. Returning to the variables $(c, c^{\Sigma^*})$ instead of $(c^*, \theta_{\text{red}})$ this model reads as

\[
\partial_t c - D \Delta c = r_s(c), \quad t \geq 0, \, z \in \Sigma,
\]

\[
e^k \cdot \partial_z c^{\Sigma^*} - e^k \cdot \text{div}_\Sigma(D^{\Sigma^*} \nabla_{\Sigma}^{\Sigma^*} c_{\text{ext}}^{\Sigma^*}) = e^k \cdot s^{\Sigma^*}(c, \theta_{\text{red}}), \quad 1 \leq k \leq n^\Sigma, \, t \geq 0, \, z \in \Sigma,
\]

\[
-D \partial_n c = s^\Sigma(c, \theta), \quad t \geq 0, \, z \in \Sigma,
\]

\[
r^\Sigma(\theta) = 0, \quad t \geq 0, \, z \in \Sigma,
\]

where $c_{\text{ext}}^{\Sigma^*} = (c_0^{\Sigma^*}, c^{\Sigma^*})^T$, $D = \text{diag}(d_i_{\text{ext}})_{i \in \mathbb{N}^N}$ and $D^{\Sigma^*} = (d_{ij}^{\Sigma^*})_{i,j \in \mathbb{N}^N}$.

From the above reasoning it should be clear how a general fast surface chemistry limit looks like:

\[
\partial_t c + \text{div} J = r(c), \quad t \geq 0, \, z \in \Sigma,
\]

\[
e^k \cdot \partial_z c^{\Sigma^*} + e^k \cdot \text{div}_\Sigma J^\Sigma = e^k \cdot s^\Sigma(c, \theta), \quad k = 1, . . . , n^\Sigma, \, t \geq 0, \, z \in \Sigma,
\]

\[
J \cdot n = s^\Sigma(c, \theta), \quad t \geq 0, \, z \in \Sigma,
\]

\[
r^\Sigma(\theta) = 0, \quad t \geq 0, \, z \in \Sigma.
\]

2.1.2. Fast sorption. Next, assume that the sorption process at the surface is considerably faster than all other physical-chemical processes, including the surface chemistry. I.e., for the characteristic parameters one has

\[
\tau_{\text{sorp}}^{\text{slow}} \ll \tau_{\text{diff},\Sigma}, \tau_{\text{react},\Sigma}^{\text{fast}}.
\]

The fast sorption limit is then obtained by first choosing $\tau_R = \tau_{R,\text{fine}} = \tau_{\text{sorp}}^{\text{slow}} \ll \tau_{\text{diff},\Sigma}, \tau_{\text{react},\Sigma}$ and multiplying equation (2) by $\tau_{\text{sorp}} > 0$ and letting formally $\tau_{\text{react},\Sigma}^{\text{fast}} \to 0$, leading to the ODE system

\[
\begin{cases}
\partial_t \mathbf{v}^{\Sigma^*}(t^*, z^*) = s^{\Sigma,*}(c^*(t^*, z^*), \theta(\Sigma, t^*, \theta^{\text{fine}}(t^*, z))) & \text{on } \Sigma, \, t^* \geq t_0^*, \\
\theta^{\text{fine}}(t_0^*, z^*) = \theta^{\text{fine,eq}}(z^*) & \text{on } \Sigma.
\end{cases}
\]

With considerations, analogous to the fast surface chemistry case, these solutions $\theta^{\text{fine}}$ tend to the (on $z \in \Sigma$ dependent) equilibrium state for the sorption processes such that $s^{\Sigma,*}(c^*(t_0^*, z^*), \theta^{\text{eq}}(z^*)) = 0$ on $\Sigma$. Returning to the coarser time scale
\[ \tau^R = \min\{\tau^{\text{react},\Sigma}, \tau^{\text{diff},\Sigma}\}, \]

the dynamics of the occupancy numbers \( \theta \) on the surface can in good approximation be replaced by the quasi-static relations

\[ s_{i}^{\Sigma,*}(c^*, \theta) = 0, \quad i = 1, \ldots, N, \quad t \geq 0, \quad z \in \Sigma. \]

Since \( \tau^{\text{sorp}} \to 0 \) and \( s_{i}^{\Sigma,*}(c^*, \theta) \to 0 \), the relation

\[ -\frac{1}{\tau^{\text{sorp}}} \partial_n c^*_i = \frac{1}{\tau^{\text{react}}} s_{i}^{\Sigma,*}(c^*, \theta) \]

cannot be used as a boundary condition in the model anymore, but

\[ \frac{1}{\tau^{\text{trans}}} d^*_i \partial_n c^*_i |_{\Sigma} \]

has to be replaced by \( \frac{1}{\tau^{\text{trans}}} d^*_i \partial_n c^*_i |_{\Sigma} \) in the dynamics of the occupancy numbers \( \theta \), so that the reduced limit model reads as

\[ \frac{1}{\tau^{R}} \partial_t c^*_i - \frac{1}{\tau^{\text{diff},\Sigma}} d^*_i \Delta^* c^*_i = \frac{1}{\tau^{\text{react}}} r^*_i(c^*) \quad \text{in} \quad (0, \infty) \times \Omega, \]

\[ \frac{1}{\tau^{R}} \partial_t \theta_i - \frac{1}{\tau^{\text{diff},\Sigma}} \text{div}_\Sigma (\sum_{j=0}^{N} d^*_i(\theta) \nabla^* \theta_j) = \frac{1}{\tau^{\text{react}}} r^*_i(\theta) \]

\[ - \frac{1}{\tau^{\text{trans}}} d^*_i \partial_n c^*_i \quad \text{on} \quad (0, \infty) \times \Sigma, \]

\[ s_{i}^{\Sigma,*}(c^*, \theta) = 0 \quad \text{on} \quad (0, \infty) \times \Sigma. \]

Returning to \( c \) and \( c^\Sigma \) instead of \( c^* \) and \( \theta \), this limit model reads as

\[ \partial_t c - D \Delta c = r(c), \quad t \geq 0, \quad z \in \Omega, \]

\[ \partial_t c^\Sigma - \text{div}_\Sigma (D^\Sigma(c^\Sigma) \nabla^\Sigma c^\Sigma_{\text{ext}})) = r^\Sigma(c^\Sigma) - D \partial_n c, \quad t \geq 0, \quad z \in \Sigma, \]

\[ s^\Sigma(c, c^\Sigma) = 0, \quad t \geq 0, \quad z \in \Sigma. \]

Alternatively, in the more general form for generic reaction, sorption and bulk and surface diffusion models,

\[ \partial_t c + \text{div} J = r(c), \quad t \geq 0, \quad z \in \Omega, \]

\[ \partial_t c^\Sigma + \text{div}_\Sigma J^\Sigma = r^\Sigma(c^\Sigma) + J^\Sigma \cdot \mathbf{n}, \quad t \geq 0, \quad z \in \Sigma, \]

\[ s^\Sigma(c, c^\Sigma) = 0, \quad t \geq 0, \quad z \in \Sigma. \]

The latter seems to be an appropriate model when considering fast sorption limits for more general reaction-diffusion-sorption models, say Maxwell-Stefan diffusion in the bulk, or more general sorption, reaction or diffusion models on the surface, e.g., more general models for the chemical potentials in the bulk and on the surface.

In fact, the limit considerably simplifies the situation for generic surface chemical potentials, cf. the following remark.

**Remark 2.4** (On the condition \( s^\Sigma(c|\Sigma; c^\Sigma) = 0 \)). For the fast surface chemistry limit it has been demonstrated that the nonlinear equilibrium condition \( r^\Sigma(c^\Sigma) = 0 \) (under mild assumptions on the structure of surface reactions) is equivalent to \( R_a(c^\Sigma) = 0 \) for all surface chemical reactions \( a \), and the latter condition can be expressed as \( A_{i}^{\Sigma} = 0 \), i.e., vanishing affinity for all surface chemical reactions.

As the sorption processes at the surface are modelled analogously to a chemical reaction \( A_{i} = A_{i}^{\Sigma} \), a similar observation can be made for the sorption equilibrium \( s^\Sigma(c|\Sigma; c^\Sigma) = 0 \), namely

\[ s^\Sigma(c|\Sigma; c^\Sigma) = 0 \Leftrightarrow \mu|_{\Sigma} = \tilde{\mu}^{\Sigma} \quad \text{on} \quad \Sigma, \]

where \( \mu = (\mu_i)_i \) and \( \tilde{\mu}^{\Sigma} = (\tilde{\mu}_i^\Sigma)_i = (\mu_i^\Sigma - \mu_i^\Sigma) \) are the vectors of bulk resp. (effective) surface chemical potentials.
condition on the adsorption and desorption velocities $R^d_i$ and $R^e_i$ for the sorption process and by the entropy production due to sorption.

2.1.4. Fast transmission between bulk phase and surface. Another limit model which can be considered (at least formally), is the limiting case for

$$
\tau^{\text{trans}} \ll \tau^{\text{diff}, \Sigma}, \tau^{\text{react}, \Sigma}, \tau^{\text{sorp}}.
$$

However, the limit model which would result has the abstract form

$$
\partial_t c + \text{div} \mathbf{J} = r(c), \quad t \geq 0, \quad \mathbf{z} \in \Omega,
$$

$$
\partial_t c^\Sigma + \text{div}_\Sigma \mathbf{J}^\Sigma = r^\Sigma(c^\Sigma) + s^\Sigma(c, c^\Sigma), \quad t \geq 0, \quad \mathbf{z} \in \Sigma,
$$

$$
\mathbf{J} \cdot \mathbf{n} = 0, \quad t \geq 0, \quad \mathbf{z} \in \Sigma,
$$

so the bulk dynamics would be completely decoupled from the surface dynamics, in the sense that the surface concentrations do not influence the reaction-diffusion system in the bulk at all. In particular, this limit case cannot be thermodynamically consistent, it even does not obey to mass conservation.
Our interpretation of this phenomenon is the following: The thermodynamic inconsistency (violation of principle of mass conservation) indicates that taking the fast transmission limit independently of other limits, is not allowed. In fact, the transmission and sorption processes are closely related, hence these sub-processes should take place on the same order of magnitude, i.e., $\tau_{\text{trans}} = \lambda \tau_{\text{sorp}}$ for some parameter $\lambda > 0$. This can be seen as a motivation for the three-parameter limit considered in subsection 2.3. In that sense, $\tau_{\text{trans}}$ is not independent of the other characteristic parameters, in particular $\tau_{\text{sorp}}$. Actually, this comes without surprise since originally the sorption rates $s_i(c, c^\Sigma)$ are just defined as the outer normal flux $-d_i \partial_n c_i$ for species $A_i$ at the boundary $\Sigma = \partial \Omega$.

2.2. Two-parameter limits. In the previous subsection, several one-parameter limits have been considered, each of them corresponding to a different thermodynamic subprocess which is assumed to take place very fast compared to all other subprocesses. Quite typically, however, not only one, but several of these thermodynamic subprocesses are very fast. For this reason, the case of two-parameter limits will be investigated next, where two of the thermodynamic subprocesses are assumed to be much faster than all the other thermodynamic subprocesses. Here, the focus lies on the fast sorption and fast surface chemistry limit, and it will also be discussed, how – if at all – a hierarchy between the speeds of these two thermodynamic mechanisms affects the resulting limit model. Hence, the following three limit cases will be studied:

(a) ultra-fast sorption and fast surface chemistry, i.e.,
\[ \tau_{\text{sorp}} \ll \tau_{\text{fast}} \ll \tau_{\text{sorp}} \ll \tau_{\text{diff}}, \tau_{\text{trans}}; \]

(b) fast sorption and ultra-fast surface chemistry, i.e.,
\[ \tau_{\text{sorp}} \ll \tau_{\text{fast}} \ll \tau_{\text{sorp}} \ll \tau_{\text{diff}}, \tau_{\text{trans}}; \]

(c) fast sorption and equivalently fast surface chemistry, i.e.,
\[ \tau_{\text{sorp}} = \lambda \tau_{\text{sorp}} \ll \tau_{\text{diff}}, \tau_{\text{trans}} \quad \text{for some fixed } \lambda > 0. \]

2.2.1. Fast surface chemistry, ultra-fast sorption. In this model one first takes the formal limit $\tau_{\text{sorp}} \to 0$, and in the resulting fast sorption limit model, i.e.,
\[ \frac{1}{\tau_R} \partial_t c_i^* - d_i^* \Delta^s c_i^* = \frac{1}{\tau_{\text{react}}} r_i^*(c^*) \quad \text{in } (0, \infty) \times \Omega, \]
\[ \frac{1}{\tau_R} \partial_t \theta_i - \frac{1}{\tau_{\text{diff}} \Sigma} \text{div}_\Sigma \left( \sum_{j=0}^N d_{ij}^* (\Sigma^* \nabla^* \theta_j) \right) = \frac{1}{\tau_{\text{react}}} r_i^* (\Sigma^*, \theta) \]
\[ - \frac{1}{\tau_{\text{trans}}} d_i^* \partial_n c_i^* \quad \text{on } (0, \infty) \times \Sigma, \]
\[ s_i^* (c^*, \Sigma^*) = 0 \quad \text{on } (0, \infty) \times \Sigma, \]
additionally considers the formal limit $\tau_{\text{react}} \to 0$. This reduces the evolutionary PDE for $\theta$ to the quasi-static relation
\[ r_i^* (\Sigma^*, \theta) = 0 \quad \text{on } (0, \infty) \times \Sigma \]
which, as for the one-parameter fast surface chemistry limit, is a condition on the part of $\theta_{\text{red}}$ lying in the linear span of $\{ \Sigma^*: a \}$. On its orthogonal complement
span\{e^k : k = 1, \ldots, n^\Sigma\}, a dynamic PDE remains, so that the resulting two-parameter limit model reads as

\[
\frac{1}{\tau_{\text{diff}}} \partial_t \cdot \mathbf{c}^e - \frac{1}{\tau_{\text{diff}}} D^* \Delta^* \mathbf{c}^e = \frac{1}{\tau_{\text{react}}} r^*(\mathbf{c}^e) \quad \text{on } (0, \infty) \times \Omega,
\]

\[
\frac{e^k_1}{\tau_{\text{diff}}} \partial_t \cdot \mathbf{c}^s - \frac{1}{\tau_{\text{trans}}} \cdot \nabla^s (\mathbf{D}^* \cdot \nabla^\Sigma \mathbf{\theta}) = - \frac{e^k_1}{\tau_{\text{trans}}} \cdot D^* \partial_n \cdot \mathbf{c}^* \quad \text{in } (0, \infty) \times \Sigma,
\]

\[
c_{\text{red}} k^\text{ad}\cdot \mathbf{c}_i^e \theta_0 - k^\text{de}\cdot \mathbf{c}_i^e \theta_1 = 0 \quad \text{in } (0, \infty) \times \Sigma,
\]

\[
r^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0 \quad \text{on } (0, \infty) \times \Sigma.
\]

This limit model will later be compared with the limit model for the other two cases.

### 2.2.2. Ultra-fast surface chemistry, fast sorption

For this situation one starts the other way round, i.e., with the fast surface chemistry model

\[
\frac{1}{\tau_{\text{diff}}} \partial_t \cdot \mathbf{c}^e = \frac{1}{\tau_{\text{react}}} r^i_1(\mathbf{c}^e), \quad t \geq 0, \ z \in \Sigma,
\]

\[
\frac{1}{\tau_{\text{diff}}} \cdot \nabla^s (\mathbf{D}^* \cdot \nabla^\Sigma \mathbf{\theta}) = \frac{e^k}{\tau_{\text{trans}}} \cdot s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}), \quad t \geq 0, \ z \in \Sigma
\]

\[
r^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0, \quad t \geq 0, \ z \in \Sigma.
\]

Inserting the third equation into the second one and multiplying the third line by \(\tau_{\text{sorp}}\), taking the formal limit \(\tau_{\text{sorp}} \to 0\) then gives

\[
\frac{1}{\tau_{\text{diff}}} \partial_t \cdot \mathbf{c}^e = \frac{1}{\tau_{\text{react}}} r^i(\mathbf{c}^e), \quad t \geq 0, \ z \in \Omega
\]

\[
\frac{e^k}{\tau_{\text{diff}}} \cdot \nabla^s (\mathbf{D}^* \cdot \nabla^\Sigma \mathbf{\theta}) = - \frac{e^k}{\tau_{\text{trans}}} \cdot (\mathbf{D}^* \cdot \nabla^\Sigma \mathbf{\theta}), \quad t \geq 0, \ z \in \Sigma
\]

\[
r^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0, \quad t \geq 0, \ z \in \Sigma,
\]

\[
s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0, \quad t \geq 0, \ z \in \Sigma.
\]

This is the same system as for the fast surface chemistry, ultra-fast sorption limit. One therefore expects the same model for equivalently fast sorption and surface chemistry as well; see the next subsection.

### 2.2.3. Equally fast surface chemistry and sorption

For this case, one starts with the full bulk-surface reaction-diffusion-sorption model (1)–(3), fixing the ratio \(\lambda = \frac{\tau_{\text{react}}}{\tau_{\text{sorp}}} > 0\). After multiplying equations (2) and (3) by \(\tau_{\text{react}} = \lambda \tau_{\text{sorp}} > 0\) and performing the formal limit \(\tau_{\text{react}} = \lambda \tau_{\text{sorp}} \to 0\), one obtains the two-parameter limit model

\[
\frac{1}{\tau_{\text{diff}}} \partial_t \cdot c_i^e - \frac{1}{\tau_{\text{diff}}} d_i^e \Delta^e c_i^e = \frac{1}{\tau_{\text{react}}} r^i_1(\mathbf{c}^e) \quad \text{in } \Omega, \ t \geq 0,
\]

\[
0 = r^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) + \lambda s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) \quad \text{on } \Sigma, \ t \geq 0,
\]

\[
0 = s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) \quad \text{on } \Sigma, \ t \geq 0.
\]

Here, the static relations

\[
r^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) + \lambda s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0 \quad \text{on } \Sigma, \ t \geq 0,
\]

\[
s^\Sigma\cdot (\mathbf{c}^e, \mathbf{\theta}) = 0 \quad \text{on } \Sigma, \ t \geq 0,
\]
are equivalent to \( s^{\Sigma,*}(c^*, \theta) = r^{\Sigma,*}(\theta) = 0 \), and this, therefore, leads to the same two-parameter limit system as before. As a result, concerning the limit model it does not matter whether the sorption or surface chemistry take place equivalently fast, or one of these processes is ultra-fast. The general form one obtains for any of the three cases is

\[
\begin{align*}
\partial_t c + \text{div } J &= r(c), & t \geq 0, \ z \in \Omega, \\
\mathbf{e}^k \cdot \partial_t c^{\Sigma} + \text{div}_\Sigma J^{\Sigma} &= \mathbf{e}^k \cdot (J \cdot \mathbf{n}), & k = 1, \ldots, n^\Sigma, \ t \geq 0, \ z \in \Sigma, \\
r^{\Sigma}(c^{\Sigma}) &= 0, & t \geq 0, \ z \in \Sigma, \\
s^{\Sigma}(c, c^{\Sigma}) &= 0, & t \geq 0, \ z \in \Sigma.
\end{align*}
\]

In this sense, the fast limits for the sorption and the surface chemistry are compatible.

### 2.2.4. Equivalent formulation of the sorption and surface chemistry equilibrium condition

In subsection 2.1.2 it has been noted that the sorption rates are modelled such that \( s_i(c, c^{\Sigma}) = 0 \) if and only if the values of the bulk and surface chemical potentials of species \( A_i \) and \( A_i^{\Sigma} \) coincide on the surface, \( \mu_i^{\Sigma} = \mu_{i|\Sigma} \). This observation may now be used to remove \( c^{\Sigma} \) from the fast-sorption, fast-surface-chemistry limit model and replace the two equilibrium conditions \( r^{\Sigma}(c^{\Sigma}) = 0 \) and \( s^{\Sigma}(c|\Sigma, c^{\Sigma}) = 0 \) by a single equilibrium condition \( r^b(c|\Sigma) = 0 \). To this end, note that by assumption 2.2 the surface chemistry only has detailed-balance equilibria and (provided \( c^\Sigma \in (0, \infty) \)), hence, \( r^{\Sigma}(c^{\Sigma}) = 0 \) if and only if \( A_\alpha^{\Sigma} = \sum_{i=1}^N \mu_{i|\Sigma} \nu_{i|\Sigma}^\Sigma = 0 \) for all surface chemical reactions \( a = 1, \ldots, m^\Sigma \). Inserting the sorption equilibrium condition \( \mu_i^{\Sigma} = \mu_{i|\Sigma} \), this means that

\[
\sum_{i=1}^N \mu_{i|\Sigma} \nu_{i|\Sigma}^\Sigma = 0, \quad a = 1, \ldots, m^\Sigma
\]

which is the equilibrium condition for the analogous set of chemical reactions in the bulk (but evaluated at the boundary \( \Sigma = \partial \Omega \)):

\[
\sum_{i=1}^N \alpha_{i|\Sigma} A_i = \sum_{i=1}^N \beta_{i|\Sigma} A_i, \quad a = 1, \ldots, m^\Sigma.
\]

Denoting the reaction rates belonging to this ensemble of bulk chemical reactions by \( r^b(c) \), the equilibrium condition \( s^{\Sigma}(c|\Sigma, c^{\Sigma}) = 0 = r^{\Sigma}(c^{\Sigma}) \) is equivalent to the nonlinear quasi-static boundary condition \( r^b(c|\Sigma) = 0 \) on \( \Sigma \).

### 2.3. Three-parameter limits

One may consider the case where not only the surface chemistry and the sorption process are ultra-fast, but the transmission between bulk and surface is fast as well, i.e.,

\[
\tau^{\text{trans}} < \tau^{\text{diff}}, \tau^{\text{sorp}} \ll \tau^{\text{react}}, \tau^{\text{sorp}} \ll \tau^{\text{slow}}, \tau^{\text{trans}} \ll \tau^{\text{diff}}.
\]

For the motivation of the fast transmission case, cf. the one-parameter limit for fast transmission in subsection 2.1.4. There it has been motivated why especially the relation \( \tau^{\text{trans}} \lesssim \tau^{\text{sorp}} \ll \tau^{\text{diff}} \) is very reasonable. As for the two-parameter limits, it is not important which of the processes is faster than the others, e.g., it does not matter whether the surface chemical reactions are fast or even ultra-fast. Therefore, it is enough to establish the model by considering the case \( \tau^{\text{trans}} \to 0 \) in
the fast sorption, fast surface reaction model, leading to $e^k \cdot (J \cdot n) = 0$ and the following reduced model

\[
\frac{1}{\tau_{\text{diff}}} D^s \Delta^s c^s = \frac{1}{\tau_{\text{react}}} r^s(c^s), \quad t \geq 0, \ z \in \Omega,
\]

\[
\frac{1}{\tau_{\text{trans}}} e^k \cdot D^s \partial_n c^s = 0, \quad k = 1, \ldots, n^\Sigma, \ t \geq 0, \ z \in \Sigma,
\]

\[
r^h \cdot (c^s|_{\Sigma}) = 0, \quad t \geq 0, \ z \in \Sigma,
\]

or, returning to the variable $c$,

\[
\partial_t c - D \Delta c = r(c), \quad t \geq 0, \ z \in \Omega,
\]

\[
e^k \cdot D \partial_n c = 0, \quad k = 1, \ldots, n^\Sigma, \ t \geq 0, \ z \in \Sigma,
\]

\[
r^h(c|_{\Sigma}) = 0, \quad t \geq 0, \ z \in \Sigma,
\]

so that, for general reaction-diffusion systems, the limit model reads as

\[
\partial_t c + \text{div } J = r(c), \quad t \geq 0, \ z \in \Omega,
\]

\[
e^k \cdot (J \cdot n) = 0, \quad k = 1, \ldots, n^\Sigma, \ t \geq 0, \ z \in \Sigma,
\]

\[
r^h(c|_{\Sigma}) = 0, \quad t \geq 0, \ z \in \Sigma.
\]

As one sees, in this reduced model, the dynamic PDE for the surface concentrations $c^\Sigma$ is fully replaced by quasi-static relations on $c$ and $J \cdot n$, so that a bulk-reaction-diffusion system with nonlinear, mixed-type boundary conditions results.

To get an idea, how for concrete reaction models the resulting PDE system and its boundary conditions look like, consider the following simple three-component model as a prototype example:

**Example 2.5 (Three component system).** Consider a three component system with no bulk chemistry and a surface reaction mechanism of the type

\[
A^\Sigma_1 + A^\Sigma_2 \rightleftharpoons A^\Sigma_3.
\]

The reaction rate is modelled by

\[
r^\Sigma(\theta) = \nu^\Sigma (\kappa^f \theta_1 \theta_2 - \kappa^b \theta_3 \theta_0),
\]

where $\nu^\Sigma = (-1, -1, 1)^T$ and $\kappa^f, \kappa^b > 0$.

Suitable conservation vectors $e^1$, $e^2$ are given by, e.g.,

\[
e^1 = (1, 0, 1)^T \quad \text{and} \quad e^2 = (0, 1, 1)^T.
\]

Moreover, the sorption rate is modelled according to the (single-site) Langmuir model

\[
s^\Sigma_i(c|_{\Sigma}, \theta) = k^\text{ad}_i c_i \theta_0 - k^\text{de}_i \theta_i, \quad i = 1, \ldots, 3.
\]

For Fickian diffusion in the bulk, the fast sorption, fast surface reaction, fast bulk-surface transport model

\[
\partial_t c + \text{div } J = r(c), \quad t \geq 0, \ z \in \Omega,
\]

\[
e^k \cdot (J \cdot n) = 0, \quad k = 1, 2, \ t \geq 0, \ z \in \Sigma,
\]

\[
r^h(c) = 0, \quad t \geq 0, \ z \in \Sigma.
\]
then takes the particular form
\[
\begin{array}{ll}
\partial_t c_i - d_i \Delta c_i = 0, & i = 1, 2, 3, t \geq 0, z \in \Omega, \\
-(d_k \partial_n c_k + d_3 \partial_n c_3) = 0, & k = 1, 2, t \geq 0, z \in \Sigma, \\
k^f \theta_1 \theta_2 - k^b \theta_3 = 0, & t \geq 0, z \in \Sigma, \\
k_i^d c_i \theta_3 - k_i^d \theta_3 = 0, & i = 1, 2, 3, t \geq 0, z \in \Sigma,
\end{array}
\]
or, after solving the latter condition for \( \mathbf{\theta}_{\text{red}} \) and inserting into the third relation:
\[
\begin{array}{ll}
\partial_t c_i - d_i \Delta c_i = 0, & i = 1, 2, 3, t \geq 0, z \in \Omega, \\
-(d_k \partial_n c_k + d_3 \partial_n c_3) = 0, & k = 1, 2, t \geq 0, z \in \Sigma, \\
c_1 c_2 - \kappa c_3 = 0, & t \geq 0, z \in \Sigma
\end{array}
\]
with \( \kappa = \frac{\kappa_1^k k_2^d k_3^d}{\kappa_1^d k_2^d k_3^d} > 0. \)

3. Mathematical analysis of a prototype model problem. This section is devoted to the three-component model problem introduced in the last section, which serves as a first example for those systems which arises from the fast-sorption–fast-surface-chemistry limit. The results on local-in-time well-posedness, positivity of solutions, blow-up criteria, and a-priori bounds will be extended to more general reaction-diffusion-sorption systems in the forthcoming paper [12].

**Model 3.1** (Three component model with chemical reactions on the surface). Let \( N = 3 \) and assume that \( r \equiv 0 \), i.e., no reactions occur within the bulk phase, whereas on the surface the following reversible chemical reaction takes place:
\[
A_1^\Sigma + A_2^\Sigma \rightleftharpoons A_3^\Sigma.
\]
In the bulk phase, diffusion is modelled by standard Fickian diffusion, leading to
\[
\begin{array}{ll}
\partial_t c_i - d_i \Delta c_i = 0, & i = 1, 2, 3, t \geq 0, z \in \Omega, \\
\end{array}
\]
with constant diffusivities \( d_i > 0, i = 1, 2, 3 \). On the surface, a fast sorption and fast reaction model with fast transport between bulk and surface is assumed, i.e.,
\[
\begin{array}{ll}
\kappa^f k_1^d k_2^d k_3^d c_1 c_2 - \kappa^b k_3^d c_3 = 0, & t \geq 0, z \in \Sigma, \\
- \mathbf{e}^k \cdot (\mathbf{D} \partial_n \mathbf{c}) = 0, & k = 1, 2, t \geq 0, z \in \Sigma,
\end{array}
\]
where \( \mathbf{e}^1 = (1, 0, 1)^T \) and \( \mathbf{e}^2 = (0, 1, 1)^T \) are the conservation vectors under the chemical reaction on the surface. This reaction has the stoichiometric vector \( \mathbf{\nu}^{\Sigma,1} = (-1, -1, 1)^T \in \mathbb{R}^3 \), and \( \mathbf{D} = \text{diag}(d_1, d_2, d_3) \in \mathbb{R}^{3 \times 3} \), so that, for \( \kappa := \frac{\kappa_1^k k_2^d k_3^d}{\kappa_1^d k_2^d k_3^d} > 0 \), the condensed form of the limit model reads as
\[
\begin{array}{ll}
\partial_t c_i - d_i \Delta c_i = 0, & i = 1, 2, 3, t \geq 0, z \in \Omega, \\
c_1 c_2 - \kappa c_3 = 0, & t \geq 0, z \in \Sigma, \\
-d_1 \partial_n c_1 - d_3 \partial_n c_3 = 0, & t \geq 0, z \in \Sigma, \\
-d_2 \partial_n c_2 - d_3 \partial_n c_3 = 0, & t \geq 0, z \in \Sigma.
\end{array}
\]

This prototype problem will be investigated here, where the first results are:
(a) Local-in-time existence and uniqueness of strong solutions to (MP) in the class $c \in W^{1,2}_p(J \times \Omega; \mathbb{R}^3)$, where $J = [0, T]$ for some $T > 0$, and $p > \frac{n+2}{2}$, is ensured, provided the initial data satisfy certain regularity and compatibility conditions. In this case, the solution depends continuously on the initial data $u_0 \in B^{-2/p}_{pp}(\Omega; \mathbb{R}^3)$.

(b) As a by-product, the construction of the strong solution provides an abstract blow-up criterion for global in time strong solutions.

(c) Moreover, for non-negative, but non-zero initial data in every component, the solution stays positive and immediately becomes strictly positive.

(d) Lastly, some a-priori bounds of type $L^\infty L^1$, $L^1 L^\infty$, $L^2 L^2$ and an entropy dissipation inequality hold true.

For the notation used here, cf. the subsection 3.2 on notation.

3.1. Some comments on the existing literature on analysis of reaction-diffusion systems. Reaction-diffusion-advection systems constitute a highly relevant and interesting research topic in mathematical modelling, mathematical analysis and numerical simulation of systems relevant for, e.g., chemical engineering. Unsurprisingly, there is abundant literature on several aspects of reaction-diffusion systems. Within this subsection, a short overview on some related results will be given. Obviously, such an overview can not be exhaustive by any means, and clearly the selection of cited papers may be biased to some extend. Here, the selection is partly based on the references given in the excellent survey by M. Pierre [43].

Without doubt, the monograph [38] of O.A. Ladyzenskaya, V.A. Solonnikov and N.N. Ural’ceva has to be included in this list, as it marks maybe the most important cornerstone for the modern theory on parabolic systems, providing $L^p$-maximal regularity and optimality for a very rich class of parabolic evolution equations. More specific on the topic of reaction diffusion equations are the by now classical books by D. Henry [35] and F. Rothe [46]. M. Pierre contributed a vast amount to the literature, e.g., [41], [42], [44], on the analysis of reaction diffusion systems, with emphasis on global existence or blow-up phenomena. Somehow related to the dimensional analysis considered here are the papers [18] and [19] by the second author and M. Pierre, where fast-reaction-limits for chemical reactions taking place on different time scales have been considered. All these references, however, have one thing in common: They all treat bulk reaction-diffusion-systems with given boundary conditions on the surface of the chemical reactor, e.g., homogeneous and non-homogeneous Dirichlet boundary conditions, Neumann boundary conditions or Robin boundary conditions.

In usually more abstract settings, H. Amann contributed an at least equally vast amount to today’s state of the art, e.g., the research papers [2]–[8], and last, but not least the monographs [9], [10].

Over the years, the abstract mathematical tools for analysing parabolic systems have considerably improved, e.g., with the theory of $R$-boundedness by E. Berkson and T.A. Gillespie [13], P. Clément et al. [23], N.J. Kalton and L. Weis [37]. For a large class of problems, applicable criteria for $L^p$-maximal regularity have been established by R. Denk, M. Hieber and the late J. Prüss [24], [25] and generalised to abstract bulk-surface type systems by R. Denk, J. Prüss and R. Zacher [27]. The latter haven been used recently by R. Schnaubelt to give abstract results on well-posedness and asymptotic behaviour of semilinear bulk-surface reaction-diffusion systems [47]. D. Bothe, M. Kähne, S. Maier and J. Saal [17] considered a
bulk-surface reaction-diffusion system with inflow and and outflow on a cylindrical domain, proving well-posedness and global existence of strong solutions. L. Desvillettes, K. Fellner and co-authors employed the entropy principle to develop a weak theory for the long-time behaviour of reaction diffusion systems; see, e.g., [28], [29], [30], [22], [31].

Note that another direction of generalisation of above results are quasilinear instead of semilinear evolution equation. As there is experimental evidence [33] that the standard Fickian diffusion model is not appropriate to describe situations of non-dilute species in a fluid mixture, and continuum-thermodynamic considerations show that these models are not thermodynamically consistent as they do not obey to the entropy principle [16], quite recently alternative models for diffusion of fluids have become more and more popular also in the mathematical community, in particular the Maxwell-Stefan approach, see, e.g., [15], [36], [48]. Furthermore, we refer to the article [20] of G. Rolland and the second author on global existence for reaction-diffusion systems with anisotropic diffusion, i.e., a diagonal diffusion matrix with entries of the form $D_i = D_i(t, z, c)$. 

3.2. Some notation and preliminaries. Throughout, $\Omega \subseteq \mathbb{R}^n$ denotes a bounded domain with compact boundary $\Sigma = \partial \Omega$ of class $C^2$, at least. Then $C(\overline{\Omega})$ denotes the space of continuous functions and, given any $k \in \mathbb{N}_0$ and $\alpha \in (0, 1]$, $C^k(\overline{\Omega})$ and $C^{k+\alpha}(\overline{\Omega})$ are the spaces of $k$-times continuously differentiable functions, respectively of $k$-times continuously differentiable functions with derivatives of order $k$ in the Hölder space $C^\alpha(\overline{\Omega})$. Moreover, given $p \in [1, \infty)$ and $\Omega \subseteq \mathbb{R}^n$ a (not necessarily bounded) Lebesgue measurable set, the Lebesgue spaces of function classes of Lebesgue measurable functions $f$ such that $\int_{\Omega} |f|^p \, dz < \infty$ is $L_p(\Omega)$, and, as usual, a function $f$ is identified with its equivalence class $[f] \in L_p(\Omega)$ of measurable functions which coincide a.e. with $f$. For $k \in \mathbb{N}_0$ or $s \in \mathbb{R}_+$, the symbols $W^s_p(\Omega)$ and $W^s_p(\Omega)$ denote the Sobolev spaces and Sobolev–Slobodetskii spaces of orders $k$ and $s$, respectively, and Besov spaces $B^s_{pp}(\Omega)$ will only be considered for the case $p = q$, noting that $B^s_{pp}(\Omega) = W^s_p(\Omega)$ for $s \in \mathbb{R}_+ \setminus \mathbb{N}_0$, but $B^k_{pp}(\Omega) \neq W^k_p(\Omega)$ for $k \in \mathbb{N}_0$. All these spaces are equipped with their standard Banach space norms $\|\cdot\|_{L_p}$, $\|\cdot\|_{C^k}$, $\|\cdot\|_{L_p}$, $\|\cdot\|_{B^s_{pp}}$ etc., and for sufficiently regular boundary there also exist their surface versions $C(\Sigma)$, $C^{k+\alpha}(\Sigma)$, $L_p(\Sigma)$, $W^k_p(\Sigma)$ etc., as well as their Banach space $E$-valued versions, e.g., $L_p(\Omega; E)$, which are Banach spaces as well. As parabolic evolution equations of second order are being considered, also the anisotropic function spaces $C^{(1,2)-(k+\alpha)}(\mathcal{J} \times \overline{\Omega}) = C^{k+\alpha,2(k+\alpha)}(\mathcal{J} \times \overline{\Omega}) := C^{k+\alpha}(\mathcal{J}; C(\overline{\Omega})) \cap L_\infty(\mathcal{J}; C^{2(k+\alpha)}(\overline{\Omega}))$, $W^{(1,2)-s}(J \times \Omega) = W_p^{(s,2s)}(J \times \Omega) = W^s_p(J; L_p(\Omega)) \cap L_p(J; W^{2s}_p(\Omega))$ for intervals $J \subseteq \mathbb{R}$, which are Banach spaces for their respective norms $\|\cdot\|_{C^{(1,2)-(k+\alpha)}}$ and $\|\cdot\|_{W^{(1,2)-s}}$, will be used.

3.3. Local-in-time existence of strong solutions for the model problem. Local-in-time existence of strong solutions can be established via the contraction mapping principle.

Theorem 3.2 (Local-in-time existence of strong solutions). Let $p > \frac{n+2}{2}$ and assume that $\Omega \subseteq \mathbb{R}^n$ is a bounded domain of class $\partial \Omega \in C^2$. Then the model problem (MP) admits a unique local-in-time strong solution which continuously depends on
the initial datum $c^0 \in B_{pp}^{2-2/p}(\Omega)$ if and only if
\[
c^0 \in I_p(\Omega) := \{c^0 \in B_{pp}^{2-2/p}(\Omega; \mathbb{R}^3_+) : \kappa c^0_1 c^0_2 - c^0_3 = 0, \\
d_i \partial_n c^0_i + d_3 \partial_n c^0_3 = 0 \ (i = 1, 2) \ \text{a.e. on } \Sigma \}\.
\]
More precisely, for every $c^* \in I_p(\Omega)$, there are $T > 0$, $\varepsilon > 0$ and $C > 0$ such that
(a) For all $c^0 \in I_p(\Omega)$ with $\|c^0 - c^*\|_{B_{pp}^{2-2/p}(\Omega)} < \varepsilon$, there is a unique strong solution $c \in W_p^{(1,2)}(J \times \Omega; \mathbb{R}^3)$ of (MP) for $J = [0,T]$.

(b) For any two initial values $c^0, c^1 \in I_p(\Omega)$ such that $\|c^0 - c^*\|_{B_{pp}^{2-2/p}(\Omega)}$ and $\|c^1 - c^*\|_{B_{pp}^{2-2/p}(\Omega)} < \varepsilon$ and the corresponding strong solutions $c, \tilde{c}$ of class $W_p^{(1,2)}(J \times \Omega; \mathbb{R}^3)$ one has
\[
\|c - \tilde{c}\|_{W_p^{(1,2)}(J \times \Omega)} \leq C \|c^0 - c^1\|_{B_{pp}^{2-2/p}(\Omega)},
\]
(c) any strong solution $c \in W_p^{(1,2)}(J \times \Omega)$ can be extended in a unique way to a maximal strong solution $c : [0,T_{\max}) \times \Omega \to \mathbb{R}^3_+$, with $c \in W_p^{(1,2)}((0,T) \times \Omega)$ for every $T \in (0,T_{\max})$.

(d) If $T_{\max} < \infty$, then $\|c(t,\cdot)\|_{B_{pp}^{2-2/p}(\Omega)} \to \infty$ as $t \nearrow T_{\max}$.

Proof. The following proof relies on a decomposition into three linear subproblems which successively can be reduced to zero initial data, and will then be solved using a fixed point argument based on the contraction mapping principle. We proceed in several steps, where the first steps allow us to construct a local-in-time strong solution $c \in W_p^{(1,2)}((0,T) \times \Omega)$ for some $T > 0$ depending on the initial datum $c^0 \in B_{pp}^{2-2/p}(\Omega; \mathbb{R}^3)$ (complying with the compatibility conditions). In the last steps we consider small admissible perturbations of the initial datum to get continuous dependence of the solution on the initial datum and, in particular, existence of a unique, maximal, i.e., non-continuable, solution, a first sufficient criterion for global existence and lower semicontinuity of the map $c^0 \mapsto T_{\max}(c^0) \in (0,\infty]$ mapping admissible initial data to the maximal existence time of their corresponding solution. Let us fix some initial data $c^0 \in B_{pp}^{2-2/p}(\Omega; \mathbb{R}^3)$ such that $-d_1 \partial_n c^0_1 = d_3 \partial_n c^0_3$ for $i = 1, 2$ and $\kappa c^0_1 c^0_2$ on $\Sigma$. Moreover, introduce an extension operator $F \in B(B_{pp}^{2-2/p}(\Omega); W_p^{(1,2)}((0,T) \times \Omega))$. Then set $f = (f_1, f_2, f_3)^T$ for $f_i := Fc^0_i \in W_p^{(1,2)}((0,T) \times \Omega)$ for $i = 1, 2, 3$ and keep in mind that $\|f_i\|_{W_p^{(1,2)}((0,T) \times \Omega)} \to 0$ for $T \to 0^+$. Observe that problem (MP) on the time interval $(0,T)$ with initial data $c(0,\cdot) = c^0$ is equivalent to the following system of scalar reaction-diffusion systems:

\[
\begin{align*}
\partial_t c_1 - d_1 \Delta c_1 &= 0 \quad \text{in } (0,T) \times \Omega, \\
-d_1 \partial_n c_1 &= g_1 \quad \text{on } (0,T) \times \Sigma, \\
c_1(0,\cdot) &= c^0_1 \quad \text{in } \Omega, \\
\partial_t c_2 - d_2 \Delta c_2 &= 0 \quad \text{in } (0,T) \times \Omega, \\
-d_2 \partial_n c_2 &= g_2 \quad \text{on } (0,T) \times \Sigma, \\
c_2(0,\cdot) &= c^0_2 \quad \text{in } \Omega, \\
\partial_t c_3 - d_3 \Delta c_3 &= 0 \quad \text{in } (0,T) \times \Omega, \\
c_3 &= h \quad \text{on } (0,T) \times \Sigma, \\
c_3(0,\cdot) &= c^0_3 \quad \text{in } \Omega
\end{align*}
\]
for \( g_1 = g_2 = d_3 \partial_n c_3 \) and \( h = \kappa^{-1} c_1 c_2 \). Fixing positive constants \( T_0, \rho_0 > 0 \), we apply the following strategy for the proof of the local well-posedness result:

1. First, using the regularity of the initial data, we reduce the problem to zero initial data, but to the price of inhomogeneities on the right hand side of the evolutionary equation in the bulk phase.

2. To the inhomogeneous problem with zero initial data, we then apply the fixed point principle, by constructing a suitable map for which fixed points are exactly the \( W^{(1,2)}_p \)-solutions of that inhomogeneous problem.

Let us consider the function \( \tilde{c} := c - f \). For \( c|_{t=0} = c^0 \), the function \( \tilde{c} \) has time trace zero \( \tilde{c}|_{t=0} = 0 \), and \( c \in W^{(1,2)}_p((0, T) \times \Omega; \mathbb{R}^3) \) is a solution to (MP-1)–(MP-3) if and only if \( \tilde{c} \in W^{(1,2)}_p((0, T) \times \Omega; \mathbb{R}^3) \) solves the inhomogeneous system with zero initial data

\[
\begin{align*}
\partial_t \tilde{c}_1 - d_1 \Delta \tilde{c}_1 &= (d_1 \Delta - \partial_t) f_1 \quad \text{in } (0, T) \times \Omega, \\
-d_1 \partial_n \tilde{c}_1 &= \tilde{g}_1 \quad \text{on } (0, T) \times \Sigma, \\
\tilde{c}_1(0, \cdot) &= 0 \quad \text{in } \Omega, \\
\partial_t \tilde{c}_2 - d_2 \Delta \tilde{c}_2 &= (d_2 \Delta - \partial_t) f_2 \quad \text{in } (0, T) \times \Omega, \\
-d_2 \partial_n \tilde{c}_2 &= \tilde{g}_2 \quad \text{on } (0, T) \times \Sigma, \\
\tilde{c}_2(0, \cdot) &= 0 \quad \text{in } \Omega, \\
\partial_t \tilde{c}_3 - d_3 \Delta \tilde{c}_3 &= (d_3 \Delta - \partial_t) f_3 \quad \text{in } (0, T) \times \Omega, \\
\tilde{c}_3 &= \hat{h} \quad \text{on } (0, T) \times \Sigma, \\
\tilde{c}_3(0, \cdot) &= 0 \quad \text{in } \Omega
\end{align*}
\]  

where the inhomogeneous right hand side \((D \Delta - \partial_t) f \in L_p((0, T) \times \Omega; \mathbb{R}^3)\), and

\[
\begin{align*}
\tilde{g}_1 &= g_1 + d_1 \partial_n f_1 = d_3 \partial_n c_3 + d_1 \partial_n f_1 = d_3 \partial_n c_3 - d_3 \partial_n f_3 + d_1 \partial_n f_1, \\
\tilde{g}_2 &= g_2 + d_2 \partial_n f_2 = d_3 \partial_n c_3 + d_2 \partial_n f_2 = d_3 \partial_n c_3 - d_3 \partial_n f_3 + d_2 \partial_n f_2, \\
\hat{h} &= g_3 - f_3 \Sigma_T = \frac{c_1 c_2}{\kappa} - f_3 \Sigma_T = \frac{1}{\kappa} (\tilde{c}_2 + f_1 \tilde{c}_2 + \tilde{c}_1 f_2 + f_1 f_2) \Sigma_T - f_3 \Sigma_T \\
\text{with } \Sigma_T := (0, T) \times \Sigma. \quad \text{One may then define for } \rho \in (0, \rho_0] \text{ and } T \in (0, T_0] \text{ the map}
\Phi = \Phi_{\rho, T} : D_0 = D_{\rho, T_0} \subseteq W^{(1,2)}_p((0, T) \times \Omega; \mathbb{R}^2) \to W^{(1,2)}_p((0, T) \times \Omega; \mathbb{R}^2)
\]

for

\[
D_0 = \{ c \in W^{(1,2)}_p((0, T) \times \Omega; \mathbb{R}^2) : c(0, \cdot) = 0, \| c \|_{W^{(1,2)}_p((0, T) \times \Omega)} \leq \rho \}
\]

as \( \Phi_1(\tilde{c}_1, \tilde{c}_2) = \phi_1(\psi(\tilde{c}_1, \tilde{c}_2)) \) which is constructed in the following way: Define \( \psi(\tilde{c}_1, \tilde{c}_2) := \tilde{c}_3 \) as the unique solution to the inhomogeneous diffusion equation (6) with data

\[
\hat{h} = \frac{1}{\kappa} [\tilde{c}_1 \tilde{c}_2 + f_1 \tilde{c}_2 + f_2 \tilde{c}_1 - \kappa f_3]_{(0,T) \times \Sigma}.
\]

Then

\[
\| \tilde{c}_3 \|_{W^{(1,2)}_p} \leq C_D \left( \| (\partial_t - d_3 \Delta) f_3 \|_{L^p} + \| \tilde{c}_1 \|_{W^{(1,2)}_p} + \| \tilde{c}_2 \|_{W^{(1,2)}_p} + \| f_1 \|_{W^{(1,2)}_p} + \| f_2 \|_{W^{(1,2)}_p} \right)
\]

\[
\leq C_D \left( \| \mathcal{F}_1 \|_{W^{(1,2)}_p} + \kappa \| \mathcal{F}_3 \|_{W^{(1,2)}_p} \right) + C \left( \| \tilde{c}_1 \|_{W^{(1,2)}_p} + \| \tilde{c}_2 \|_{W^{(1,2)}_p} + \| f_1 \|_{W^{(1,2)}_p} + \| f_2 \|_{W^{(1,2)}_p} \right)
\]
with constants $C_D, C > 0$. These can be chosen independently of $T \in (0, T_0)$ as $\hat{h}_i|_{t=0} = 0$ and $\hat{c}_1(0, \cdot) = 0$, and $\| \cdot \|_{W_p^{1,2}}$ denotes $\| \cdot \|_{W_p^{1,2}(0,T) \times \Omega}$. This can be seen, e.g., by mirroring in time direction and zero extension, e.g.,
\[
\hat{H}(t, \cdot) := \begin{cases} 
\hat{h}(t, \cdot), & t \in [0, T], \\
\hat{h}(t - T, \cdot), & t \in [T, 2T], \\
0, & t > 2T
\end{cases}
\]
and using $L_p$-optimality and Sobolev-Murray estimates on the (fixed) time interval $(0, T_0)$. The functions $\phi_i(\hat{c}_3) \in W_p^{1,2}(0, T) \times \Omega$ are then defined as the solutions to the boundary problems (4)--(5) for the boundary inhomogeneities
\[
\begin{align*}
\hat{g}_1 &= d_3 \partial_n \hat{c}_3 - d_3 \partial_n f_3 + d_1 \partial_n f_1, \\
\hat{g}_2 &= d_3 \partial_n \hat{c}_3 - d_3 \partial_n f_3 + d_2 \partial_n f_2.
\end{align*}
\]
Using the $L_p$-optimal estimates for the inhomogeneous Neumann problem, these solutions are unique and satisfy
\[
\begin{align*}
\| \phi_i(\hat{c}_3) \|_{W_p^{1,2}} &\leq C_N \left( \| \partial_i - d_i \Delta \|_{L_p} + |d_3 \partial_n \hat{c}_3 - d_3 \partial_n f_3 + d_1 \partial_n f_1| \right) \\
&\leq C_N \left( \| f_1 \|_{W_p^{1,2}} + |f_3 \|_{W_p^{1,2}} + |\hat{c}_3 \|_{W_p^{1,2}} \right) \\
&\leq C_N \left( \| \mathcal{F}_{\alpha_1} \|_{W_p^{1,2}} + \| \mathcal{F}_{\alpha_3} \|_{W_p^{1,2}} \\
&+ C_D \left( \| \mathcal{F}_{\alpha_3} \|_{W_p^{1,2}} + C \left( \| \hat{c}_1 \|_{W_p^{1,2}} \| \hat{c}_2 \|_{W_p^{1,2}} \right) \\
&+ \| \mathcal{F}_{\alpha_3} \|_{W_p^{1,2}} \| \hat{c}_2 \|_{W_p^{1,2}} + \| \hat{c}_1 \|_{W_p^{1,2}} \| \mathcal{F}_{\alpha_3} \|_{W_p^{1,2}} \right) \right)
\end{align*}
\]
where again $C_N > 0$ is independent of $T \in (0, T_0)$ thanks to $\phi(\hat{c}_3)|_{t=0} = 0$. Now, choosing $\rho \in (0, \rho_1] \subseteq (0, \rho_0]$ small enough, i.e., $CC_NC_D < 1$ and afterwards choosing $T \in (0, T_1) \subseteq (0, T_0]$, i.e., such that the sum of the remaining terms are less or equal $\rho(1 - C_NC_D \rho_1)$ for any $\| \hat{c}_i \|_{W_p^{1,2}(0,T) \times \Omega} \leq \rho$, one finds that
\[
\| \Phi_i(\hat{c}_1, \hat{c}_2) \| = \| \phi_i(\hat{c}_3) \| \leq \rho \quad \text{for all } (\hat{c}_1, \hat{c}_2)^T \in D_{\rho,T_0}, \rho \in (0, \rho_1], T \in (0, T_1],
\]
i.e., $\Phi : D_{T,\rho,0} \rightarrow D_{T,\rho,0}$ for all these $\rho, T$. It remains to show that $\Phi : D_{T,\rho,0} \rightarrow D_{T,\rho,0}$ is a strict contraction when choosing $T, \rho > 0$ sufficiently small. Thus, consider $(\hat{c}_1, \hat{c}_2)^T, (\tilde{c}_1, \tilde{c}_2)^T \in D_{\rho,T,0}$. Then $\psi(\hat{c}_1, \hat{c}_2) - \psi(\tilde{c}_1, \tilde{c}_2)$ solves (6) for
\[
f_3 = 0, \quad \hat{h} = \hat{c}_1 \hat{c}_2 - \hat{c}_1 \hat{c}_2 + f_1(\hat{c}_2 - \hat{c}_2) + f_2(\hat{c}_1 - \hat{c}_1)
\]
and thus
\[
\| \psi(\hat{c}_1, \hat{c}_2) - \psi(\tilde{c}_1, \tilde{c}_2) \|_{W_p^{1,2}} \leq C_D \| \hat{c}_1 \hat{c}_2 - \tilde{c}_1 \tilde{c}_2 + f_1(\hat{c}_2 - \hat{c}_2) + f_2(\hat{c}_1 - \hat{c}_1) \|_{W_p^{1,2}} \\
\leq CC_D \left( \| \hat{c}_1 - \tilde{c}_1 \|_{W_p^{1,2}} \| \hat{c}_2 \|_{W_p^{1,2}} - \| \tilde{c}_1 \|_{W_p^{1,2}} \| \hat{c}_2 - \tilde{c}_2 \|_{W_p^{1,2}} \\
+ \| f_1 \|_{W_p^{1,2}} \| \hat{c}_2 - \tilde{c}_2 \|_{W_p^{1,2}} + \| f_2 \|_{W_p^{1,2}} \| \hat{c}_1 - \tilde{c}_1 \|_{W_p^{1,2}} \right)
\]
and then one obtains in similar fashion that
\[
\begin{align*}
\| \phi_i(\hat{c}_1, \hat{c}_2) - \phi_i(\tilde{c}_1, \tilde{c}_2) \|_{W_p^{1,2}} &= \| \phi_1(\psi(\hat{c}_1, \hat{c}_2)) - \phi_1(\psi(\tilde{c}_1, \tilde{c}_2)) \|_{W_p^{1,2}} \\
&\leq C_D \| \psi(\hat{c}_1, \hat{c}_2) - \psi(\tilde{c}_1, \tilde{c}_2) \|_{W_p^{1,2}} \\
&\leq CC_N C_D \left( \| \hat{c}_1 - \tilde{c}_1 \|_{W_p^{1,2}} \| \hat{c}_2 \|_{W_p^{1,2}} - \| \tilde{c}_1 \|_{W_p^{1,2}} \| \hat{c}_2 - \tilde{c}_2 \|_{W_p^{1,2}} \\
+ \| f_1 \|_{W_p^{1,2}} \| \hat{c}_2 - \tilde{c}_2 \|_{W_p^{1,2}} + \| f_2 \|_{W_p^{1,2}} \| \hat{c}_1 - \tilde{c}_1 \|_{W_p^{1,2}} \right).
\end{align*}
\]
Choosing \( \rho \in (0, \rho_1) \), \( T \in (0, T_1) \) sufficiently small, the terms \( \| \tilde{c}_1 \|_{W^{1,2}_p}, \| \tilde{c}_2 \|_{W^{1,2}_p}, \| f_i \|_{W^{1,2}_p} \) become uniformly small, independently of the choice \( (\tilde{c}_1, \tilde{c}_2)^T, (c_1, c_2)^T \in D_{T, \rho, 0} \), and hence \( \rho, T \) may be chosen such that \( \Phi \) is a strict contraction on \( D_{\rho, T, 0} \). As \( D_{T, \rho, 0} \) is a complete metric space as a closed subset of the anisotropic Sobolev space \( W^{1,2}_p((0, T) \times \Omega) \), by Banach’s fixed point theorem \( \Phi \) has a unique fixed point \( (\tilde{c}_1, \tilde{c}_2) \in D_{\rho, T, 0} \), and then for \( \hat{c}^* := (\tilde{c}_1^*, \tilde{c}_2^*, \psi(\tilde{c}_1^*, \tilde{c}_2^*)) \) the function \( c := f + \hat{c}^* \) is the unique \( W^{1,2}_p \)-solution to \( (\text{MP}) \) with initial data \( c|_{t=0} = c^0 \).

So far, the proof does neither show continuous dependence on the data nor does it provide any blow-up criterion. To this end, let us fix some admissible initial datum \( c^{*, 0} \in B^{2-2/p}_p(\Omega; \mathbb{R}^3) \) and let \( c^* \in W^{1,2}_p((0, T) \times \Omega) \) be the corresponding solution existing at least on some time interval \( (0, T) \) which is fixed from now on.

Consider the extension operator \( \mathcal{F} \) as a bounded linear operator \( \mathcal{F} : B^{2-2/p}_p(\Omega) \to W^{1,2}_p((0, T) \times \Omega) \), and let \( r \in (0, r_0) \) for some fixed \( r_0 > 0 \). Consider any admissible (i.e., complying with the compatibility conditions) initial datum \( c^{0, 0} \in B_r(c^{*, 0}) \subseteq B^{2-2/p}_p(\Omega; \mathbb{R}^3) \) and for \( c \in W^{1,2}_p((0, T) \times \Omega; \mathbb{R}^3) \) with \( c(0, \cdot) = c^0 \) set \( \delta c := c - c^* \in W^{1,2}_p((0, T) \times \Omega; \mathbb{R}^3) \) and \( \delta c^{0} = c^0 - c^{*, 0} \in B_r(0) \subseteq B^{2-2/p}_p(\Omega; \mathbb{R}^3) \). Then \( c \) is the \( W^{1,2}_p \)-solution to \( (\text{MP}) \) if and only if only \( \delta c \) solves

\[
\begin{align*}
(\partial_t - D\Delta)\delta c &= 0 \quad \text{in } (0, T) \times \Omega, \\
-d_1 \partial_n \delta c_1 - d_2 \partial_n \partial_t \delta c_2 &= d_3 \partial_n \delta c_3 \quad \text{on } (0, T) \times \Sigma, \\
\kappa \delta c_3 &= \delta c_1 \cdot \delta c_2 + c_2^* \delta c_1 + c_1^* \delta c_2 \quad \text{on } (0, T) \times \Sigma, \\
\delta c(0, \cdot) &= \delta c^{0} \quad \text{in } \Omega.
\end{align*}
\]

This problem is very similar to the model problem \( (\text{MP}) \) itself, and with a similar technique as above it can be shown that for \( r \in (0, r_0) \) and \( \rho \in (0, \rho_0) \) sufficiently small it admits a unique solution \( \delta c \in W^{1,2}_p((0, T) \times \Omega) \) with \( \| \delta c \|_{W^{1,2}_p} \leq \rho \) to any admissible initial datum \( \delta c^{0} \in B_r(0) \subseteq B^{2-2/p}_p(\Omega; \mathbb{R}^3) \). This gives continuous dependence of the solution on the initial data \( c^{0, 0} \in B^{2-2/p}_p(\Omega; \mathbb{R}^3) \). At the same time, this implies in particular that for any admissible initial data \( c^{0, 0} \in B^{2-2/p}_p(\Omega; \mathbb{R}^3) \) with \( \| c^{0, 0} \|_{B^{2-2/p}_p} \leq \rho \) the corresponding solution exists at least on some time interval \( (0, T_\rho) \) with \( T_\rho > 0 \) independent on the particular choice of the initial datum. Hence, by time-invariance of the model problem \( (\text{MP}) \), any solution \( c \in W^{1,2}_p((0, T_{\max}) \times \overline{\Omega}) \) such that \( \sup_{t \in (0, T_{\max})} \| c(t, \cdot) \|_{B^{2-2/p}_p(\Omega)} < \infty \) exists globally, i.e., \( T_{\max} = \infty \). Then, also the map \( \delta c^{0} \mapsto T_{\max}(\delta c^{0}) \) defined on the set of admissible initial data in \( B^{2-2/p}_p(\Omega; \mathbb{R}^3) \) is lower semi-continuous.

3.4. Classical solutions. For Fickian type reaction-diffusion systems with homogeneous Dirichlet or Neumann boundary data, it is well known that these systems have the property of instantaneous smoothing, e.g., for the homogeneous heat equation with no-flux boundary conditions

\[
\begin{align*}
\partial_t \vartheta - \Delta \vartheta &= 0 \quad \text{in } (0, T) \times \Omega, \\
\partial_n \vartheta &= 0 \quad \text{on } (0, T) \times \Sigma, \\
\vartheta(0, \cdot) &= \vartheta^0 \in B^{2-2/p}_p(\Omega)
\end{align*}
\]

for some \( p > 1 \) and \( \Omega \) a bounded domain with \( C^\infty \)-boundary, one has the regularity \( \vartheta \in C((0, T); C^\infty(\bar{\Omega})) \), or, if \( \partial \Omega \) is merely of class \( \partial \Omega \in C^{k+\alpha} \) for some \( k \in \mathbb{N}_0 \).
and \( \alpha \in (0,1), \vartheta \in C((0,T); C^{k+\alpha}(\overline{\Omega})) \). This essentially follows from a bootstrap-type argument, optimal regularity results in the spaces \( L^p(\Omega) \) \((p \in (1,\infty))\) and \( C^\alpha(\overline{\Omega}) \) \((\alpha \in (0,1))\), and the Sobolev-Morrey-embeddings for regular bounded domains. In the case of inhomogeneous boundary data such a smoothing cannot be observed, as by the optimality results on parabolic evolution equations with inhomogeneous boundary data, the boundary data a priori need to satisfy the required regularity conditions in the optimality results. Therefore, one can only expect the solution \( c \) to lie in the class \( c \in W^{(1,2)}_p((0,T) \times \Omega; \mathbb{R}^3) \) if \( c^0 \in B^{2-2/p}_p(\Omega; \mathbb{R}^3) \). On the other hand, for \( \Omega \) being a bounded \( C^{2+\alpha} \)-domain and initial data in the class \( C^{2+\alpha}(\Omega; \mathbb{R}^3) \) (and subject to the compatibility conditions at the boundary), one would expect the solution \( c \) to lie in the class \( c \in C^{(1,2)-(1+\alpha/2)}([0,T] \times \Omega; \mathbb{R}^3) = C^{1+\alpha/2}([0,T]; C((\Omega; \mathbb{R}^3)) \cap L_\infty([0,T]; C^{2+\alpha}(\Omega; \mathbb{R}^3)) \).

### Proposition 3.3 (Local-in-time existence of classical solutions)

Let \( \Omega \subseteq \mathbb{R}^n \) be a bounded domain of class \( \partial \Omega \in C^{2+\alpha} \) for some \( \alpha \in (0,1) \). If \( c^0 \in C^{2+\alpha}(\Omega; \mathbb{R}^3) \) satisfies the compatibility conditions \( \kappa c^0 \big|_\Sigma = (d_0^{(0)})\big|_\Sigma \) and \( -d_1 \partial_n c^0 \big|_\Sigma = -d_2 \partial_n c^0 \big|_\Sigma = d_3 \partial_n c^0 \big|_\Sigma \) on \( \Sigma \), and the boundary values of the initial data are sufficiently small in \( L_\infty(\Sigma; \mathbb{R}^3) \)-norm, then there is \( T > 0 \) and a unique solution \( c \in C^{1+\frac{\alpha}{2}+\alpha}(([0,T] \times \Omega; \mathbb{R}^3) \) of (MP), and it coincides with the \( W^{(1,2)}_p \)-solutions for \( p \in (1,\infty) \).

We will not give a full prove here, but only comment on approaches towards improving local-in-time existence of classical solutions. As already noted, such existence results cannot simply be derived from a smoothing effect (which we do not have globally here, but only smoothing in the interior \( \Omega \), i.e., smoothness of the solutions in \((0,T) \times \Omega \)). Instead, one may repeat the existence proof as in the \( L^p \)-setting, i.e., consider initial data \( c^0 \in C^{2+\alpha}(\overline{\Omega}) \) such that the compatibility conditions \( -d_1 \partial_n c^0 = -d_2 \partial_n c^0 = d_3 \partial_n c^0 \) as well as \( \kappa c^0 = c^0 c^0 \) are satisfied on \( \Sigma \). One may then try to decompose the system into three scalar subproblems (MP-1)-(MP-3), analogously to the existence proof in the \( L^p \)-setting. The map \( \Phi \) for which one seeks a fixed point corresponding to a classical solution \( c \in C^{1+\alpha/2,2+\alpha}([0,T] \times \overline{\Omega}; \mathbb{R}^3) \), may then be defined on a complete metric space

\[
D_0 \subseteq \{ c \in C^{1+\alpha/2,2+\alpha}([0,T] \times \overline{\Omega}) : c(0,\cdot) = 0 \}.
\]

Using optimal Hölder estimates for the inhomogeneous Dirichlet and Neumann problems for the diffusion equation, and employing interpolation inequalities for functions \( f \in C^{1+\alpha/2,2+\alpha}([0,T] \times \overline{\Omega}) \) with \( f(0,\cdot) = 0 \), one can then show that \( \Phi \) is a strict contraction \( \Phi : D_0 \to D_p \), provided

\[
C_p + C'(T) + C \|c^0\|_\infty < 1,
\]

where \( C > 0 \) and \( C'(T) \to 0 \) as \( T \to 0^+ \). Clearly, for small initial data measured in terms of \( \|c^0\|_\infty \) such a choice of \( T, \rho > 0 \) is possible, which gives local-in-time existence of classical solutions for sufficiently regular data, provided the initial data are small in supremum norms. Clearly, the latter is very unsatisfactory, and we are confident that this smallness condition is unnecessary, i.e., can be dropped. The problem rather lies in the technique used for the proof, more precisely the decomposition into three (quite easy to handle) scalar subproblems (MP-1)-(MP-3). Comparing our proof with the techniques used in \([39, \text{section } 8.5.4] \) (or, \([1]\)) for quite general scalar nonlinear parabolic problems with nonlinear boundary conditions, one finds that the approach used there should help to get rid of the smallness
condition on \(\|c^0\|_{\infty}\). First note, however, that the results from there cannot directly be applied to the situation considered here: On the one hand, in [39, section 8.5.4] scalar equations are being considered and, more even important, the results are formulated for oblique boundary conditions under the non-tangentiality condition. The prototype fast-surface-limit model (MP), however, has boundary conditions of mixed orders (flux-coupling conditions \(-d_1\partial_n c_1 = -d_2\partial_n c_2 = d_3\partial_n c_3\), i.e., first order type boundary conditions, plus a nonlinear Dirichlet coupling-condition \(\kappa c_1 = c_1 c_2\), i.e., a zero order boundary condition). Using a linearisation technique analogous to the technique used in [39, section 8.5.4] hints that one should consider a linearised version of the fast-surface limit model (MP) of the form

\[
\begin{align*}
\partial_t c - D \Delta c &= f & \text{in } (0, \infty) \times \Omega, \\
-d_1\partial_n c_1 - d_3\partial_n c_3 &= g_1 & \text{on } (0, \infty) \times \Sigma, \\
-d_2\partial_n c_2 - d_3\partial_n c_3 &= g_2 & \text{on } (0, \infty) \times \Sigma, \\
\kappa c_1 - c_1^0 c_2 - c_2^0 c_3 &= h & \text{on } (0, \infty) \times \Sigma, \\
c(0, \cdot) &= c^0 & \text{on } \overline{\Omega}
\end{align*}
\]

and one has to show that this system has optimal H"older regularity, i.e., for every \(f \in C^{\alpha/2, \alpha}((0, T) \times \overline{\Omega}; \mathbb{R}^3)\), \(g_1, g_2 \in C^{(1+\alpha)/2, 1+\alpha}((0, T) \times \Sigma), h \in C^{1+\alpha/2, 2+\alpha}((0, T) \times \Sigma)\) and \(c^0 \in C^{2+\alpha}(\overline{\Omega})\), there is a unique solution \(c \in C^{1+\alpha/2, 2+\alpha}((0, T) \times \overline{\Omega}; \mathbb{R}^3)\) which depends continuously on the data, in the sense that

\[
\|c\|_{C^{1+\alpha/2, 2+\alpha}} \leq C \left( \|f\|_{C^{\alpha/2, \alpha}} + \|g\|_{C^{(1+\alpha)/2, 1+\alpha}} + \|h\|_{C^{1+\alpha/2, 2+\alpha}} + \|c^0\|_{C^{2+\alpha}} \right)
\]

with some \(C > 0\). To our knowledge, for general systems with mixed type of boundary conditions such optimality results have not been stated explicitly in the literature, except for [1], [49], where results on systems with boundary conditions of mixed type have been announced, but actually not been proven. Based on the fact that in the \(L^p\)-setting such an extension of \(L^p\)-maximal regularity results is possible, when modifying the proofs for abstract \(L^p\)-maximal regularity results, we strongly believe that such Schauder-type estimates can be derived as well, cf. the upcoming research paper [12]. Then, the fixed point procedure could be applied in a metric space

\[
D_0 \subseteq \{ c \in C^{1+\alpha/2, 2+\alpha}((0, T) \times \overline{\Omega}) : c(0, \cdot) = 0 \}
\]

and \(C^{\alpha/2, \alpha}\)-maximal regularity in connection with interpolation inequalities for functions \(f\) in the class \(C^{1+\alpha/2, 2+\alpha}((0, T) \times \overline{\Omega})\) would provide a unique local-in-time classical solution \(c \in C^{1+\alpha/2, 2+\alpha}((0, T) \times \overline{\Omega}; \mathbb{R}^3)\) without any smallness condition on the initial data \(c^0 \in C^{2+\alpha}(\overline{\Omega}; \mathbb{R}^3)\), complying to the compatibility conditions \(-d_1\partial_n c_1^0 = -d_2\partial_n c_2^0 = d_3\partial_n c_3^0\) and \(\kappa c_1^0 = c_1^0 c_2^0\) on \(\Sigma\) of the latter.

### 3.5. Positive invariance for the model problem

In the previous sections, we have shown that for any initial data \(c^0 \in B^{2(p-2)/p}_{\infty,p}(\Omega; \mathbb{R}^3)\) satisfying the compatibility conditions and for \(p > \frac{n+2}{2}\), there is a unique solution \(c \in W_p^{(1,2)}((0, T) \times \Omega; \mathbb{R}^3)\). This can be extended to a non-continuable maximal solution \(c : (0, T_{\max}) \times \Omega \to \mathbb{R}^3\), where either \(T_{\max} = \infty\), or \(\|c(t, \cdot)\|_{B^{2(p-2)/p}_{\infty,p}(\Omega; \mathbb{R}^3)}\) blows up in finite time as \(t \nearrow T_{\max}\). To have a physically relevant model, however, one aims for positivity of solutions: As \(c\) models a vector of molar concentrations, only \(c_i(t, z) \geq 0\) for all \(t \geq 0\) and \(z \in \overline{\Omega}\) is physically significant, and, in particular, for non-negative initial data, the solution should stay non-negative for all times \(t \in (0, T_{\max})\).
Proposition 3.4 (Positive invariance). Let \( p > \frac{q}{2}, \Omega \subseteq \mathbb{R}^n \) be a bounded domain of class \( C^{2+\alpha} \), let \( 0 \leq c_0 \in C^{2+\alpha}(\overline{\Omega}; \mathbb{R}^N) \) satisfy the compatibility conditions for (MP) and \( c \in C^{1+\alpha/2+\alpha}(0, T) \times \overline{\Omega}; \mathbb{R}^N) \) be a classical solution to (MP). Then either \( c = (c_1, c_2, 0) \) where \( c_1 \equiv 0 \) and \( c_2(t, \cdot) = e^{t \Delta} c_0 \) or \( c_1(t, \cdot) = e^{t \Delta} c_0 \) (with \( e^{t \Delta} \) denoting the Neumann heat semigroup) and \( c_2 \equiv 0 \), or \( c(t, z) \in (0, \infty)^3 \) for all \( t \in (0, T) \) and \( z \in \overline{\Omega} \).

Proof. The proof of this positivity result is organized as follows:

1. First, we show that for non-negative initial data, classical solutions stay non-negative by considering perturbed, strictly positive initial data and positive perturbation on the right-hand side of the bulk evolutionary equation in (MP).
2. Secondly, we employ the strong maximum principle and the parabolic boundary value lemma to show that the component functions \( c_i, i = 1, 2, 3 \), either are identically zero for all times \( t \geq 0 \) or strictly positive for all times \( t > 0 \).

Fix a classical solution \( c \in C^{1+\alpha/2+\alpha}(0, T) \times \overline{\Omega} \) and any \( T \in (0, T_{\text{max}}) \). It suffices to prove the assertion for this fixed, but arbitrary \( T \). We start by showing that \( c \geq 0 \) on \([0, T] \times \overline{\Omega}\) and for this purpose consider for sufficiently small \( \varepsilon > 0 \) the positively perturbed problem

\[
\begin{align*}
\left\{ \begin{array}{ll}
(\partial_t - d_i \Delta) c_i^{\varepsilon} &= \varepsilon & \text{in } [0, T] \times \Omega, \ i = 1, 2, 3, \\
-d_i \partial_n c_i^{\varepsilon} &= -d_2 \partial_n c_2^{\varepsilon} = d_3 \partial_n c_3^{\varepsilon} & \text{on } [0, T] \times \Sigma, \\
c_1^{\varepsilon} c_2^{\varepsilon} &= \kappa c_3^{\varepsilon} & \text{on } [0, T] \times \Sigma, \\
c^{\varepsilon}(0, \cdot) &= c^{\varepsilon, 0} & \text{on } \overline{\Omega}
\end{array} \right.
\]

for initial data \( c^{\varepsilon, 0} \geq c_0^{\varepsilon, 0} \geq c_0^0 + \varepsilon > 0 \) of class \( C^{2+2\alpha} \) and satisfying the compatibility conditions at the boundary. Such initial conditions can be constructed as follows. Take \( c_i^{\varepsilon, 0} = c_i^0 + \varepsilon \) for \( i = 1, 2 \) and make the ansatz \( c_3^{\varepsilon, 0} = c_0^0 + \varepsilon \phi_1 + \varepsilon^2 \phi_2 \) for functions \( \phi_1, \phi_2 \in C^{2+\alpha}(\overline{\Omega}) \). To comply with the compatibility conditions at the boundary, one needs to have

\[
\begin{align*}
\partial_n \phi_1 &= \partial_n \phi_2 = 0 & \text{on } \Sigma, \\
\varepsilon \phi_1 + \varepsilon^2 \phi_2 &= \varepsilon(c_0^0 + c_0^0 + \varepsilon^2) & \text{on } \Sigma,
\end{align*}
\]

and the latter decouple, if we want to choose \( \phi_1 \) and \( \phi_2 \) independent from \( \varepsilon > 0 \). Thus, we may choose \( \phi_2 = \frac{1}{\varepsilon} \) and it remains to construct \( \phi_1 \in C^{2+\alpha}(\overline{\Omega}) \) such that

\[
\begin{align*}
\phi_1 &\geq 0 & \text{in } \overline{\Omega}, \\
\partial_n \phi_1 &= 0 & \text{on } \Sigma, \\
\kappa \phi_1 &= c_0^0 + c_0^0 & \text{on } \Sigma.
\end{align*}
\]

Once such a function \( \phi_1 \) has been found, repeating the construction of classical (Hölder regular) solutions, one finds that at least for sufficiently small \( \varepsilon > 0 \) these problems admit a unique classical solution \( c^\varepsilon \in C^{1,2+\alpha}(0, T) \times \overline{\Omega} \) and these tend to \( c \in C^{1,2+\alpha}(0, T) \times \overline{\Omega} \) for \( \varepsilon \to 0^+ \). To show that \( c \geq 0 \), it thus suffices to show \( c^\varepsilon > 0 \) for all \( \varepsilon > 0 \) for which the classical solution exists and is unique. In fact, it suffices to show this strict positivity on \([0, T] \times \overline{\Omega}\). Thus, set

\[
t_0^\varepsilon := \sup\{t \in [0, T] : c^\varepsilon(s, \cdot) > 0 \text{ for all } s \in [0, t]\}.
\]

We are done, if we can establish \( t_0^\varepsilon = T \). Therefore, assume that \( t_0^\varepsilon \) were strictly smaller than \( T \). Since the initial data are uniformly strictly positive, we can exclude the possibility that \( t_0^\varepsilon = 0 \) from continuity of the solution. Thus \( t_0 := t_0^\varepsilon \in (0, T) \).
and there are \( i_0 \in \{1, 2, 3\} \) and \( z_0 \in \Omega \) such that \( c_{i_0}^ε(t_0, z_0) = 0 \) and, in particular, \( \partial_{t_i} c_{i_0}^ε(t_0, z_0) \leq 0 \).

First, we show that \( c_i^ε(t_0, \cdot) > 0 \) in \( \Omega \): Could \( z_0 \) be chosen to lie in \( \Omega \), then
\[
-d_{i_0} \Delta c_{i_0}^ε(t_0, z_0) = -\partial_{t_i} c_{i_0}^ε(t_0, z_0) + \varepsilon \geq \varepsilon > 0
\]
and, hence, \(-d_{i_0} \Delta c_{i_0}^ε(t_0, \cdot) > 0 \) in some sufficiently small ball \( B_\eta(z_0) \) and at the same time \( c_{i_0}^ε(t_0, z_0) = 0 = \min_{B_\eta(z_0)} c_{i_0}^ε(t_0, \cdot) \), contradicting the strict elliptic maximum principle. Thus \( c_i^ε(t_0, \cdot) > 0 \) in \( \Omega \) for \( i = 1, 2, 3 \).

However, \( c_i^ε(t_0, z_0) = 0 \) for some \( z_0 \in \Sigma \) while \( c^ε(t_0, \cdot) > 0 \) in \( \Omega \) contradicts the boundary conditions imposed: In fact, from the boundary condition \( (c_i^ε c_j^ε)(t_0, z_0) = \kappa c_3^ε(t_0, z_0) \), it follows that there is \( i_1 \neq i_0 \) such that either \( i_0 \) or \( i_1 \) equals 3 and \( c_i^ε(t_0, z_0) = 0 \) as well. Moreover, \(-d_{i_0} \partial_n c_{i_0}(t_0, z_0) = +d_{i_1} \partial_n c_{i_1}^ε(t_0, z_0) \), but as \( c_{i_0}, c_{i_1} > 0 \) on \([0, t_0] \times \Omega \), the parabolic boundary value lemma (see [45, Theorem 3.6]) gives that both \(-d_{i_0} \partial_n c_{i_0}(t_0, z_0), -d_{i_1} c_{i_1}(t_0, z_0) > 0 \) are strictly positive, a contradiction!

Together, these observations show that \( c_i^ε > 0 \) on \([0, T] \times \Omega \) for all \( i = 1, 2, 3 \) and \( \varepsilon > 0 \). Letting \( \varepsilon \to 0^+ \) then shows that \( c \geq 0 \) on \([0, T] \times \Omega \) and, hence, on \([0, T_{\text{max}}] \times \Omega \).

Secondly, we show that \( c > 0 \) on \((0, T_{\text{max}}] \times \Omega \) or at least two of the initial data \( c_1^0, c_2^0 \) and \( c_3^0 \), one of them being \( c_3^0 \), are identically zero, and in the latter case the solution of (MP) is given by the Neumann heat semigroup \( c_i(t, \cdot) = e^{d_1 \Delta t} c_i^0 \).

Fact I: If \( c_{i_0}(t_0, z_0) = 0 \) for some \( i_0 \in \{1, 2, 3\} \), \( t_0 > 0 \) and \( z_0 \in \Omega \), then \( c_{i_0} \equiv 0 \) on \([0, t_0] \times \Omega \) by the strict parabolic maximum principle.

Fact II: If \( c_{i_0} > 0 \) on \([0, t_0] \times \Omega \) for some \( i_0 \in \{1, 2, 3\} \), \( t_0 > 0 \), then \( c_{i_0} > 0 \) on \([0, T_{\text{max}}] \times \Omega \). Similar to showing strict positivity of \( c^ε \) above, this follows using fact I, the boundary conditions and the parabolic boundary value lemma [45, Theorem 3.6].

Fact III: Combining facts I and II, we conclude that only the following four cases are possible: \( c > 0, c \equiv 0, c_1 = c_3 \equiv 0 \) and \( c_2 > 0 \), or \( c_1 > 0 \) and \( c_2 = c_3 \equiv 0 \) on \((0, T] \times \Omega \). In the latter cases, e.g., the last case, \( c_1(t, \cdot) = e^{d_1 \Delta t} c_1^0 \), where \((e^{d_1 \Delta t})_{t \geq 0} \) denotes the analytic semigroup generated by \( d_1 \) times the Neumann Laplace operator as \(-d_1 \partial_n c_1 = d_2 \partial_n c_3 = 0 \) on \([0, T] \times \Sigma \). This follows from uniqueness of the solution to (MP).

3.6. A-priori bounds on the strong solution of the fast sorption-fast-surface-chemistry model. By Theorem 3.2, a bound on the phase space norm \( \|\cdot\|_{L^p(\Omega)} \) is enough for establishing global existence of a strong solution. To derive such a bound, is a delicate matter and it is actually unclear how to achieve this. On the other hand, for some weaker norms a-priori bounds are valid for free. The derivation of these is based on the parabolic maximum principle and entropy considerations, highlighting the fruitful interplay between mathematical modelling, analysis and physics.

**Theorem 3.5 (A-priori bounds).** Let the initial datum \( c^0 \in L^p(\Omega) \cap C^2(\Omega; \mathbb{R}^N) \) be given and \( c \in C^{0,1}(\{0, T_{\text{max}}\} \times \Omega; \mathbb{R}^N_-) \) be a maximal classical solution to the
fast-surface-chemistry, fast-sorption, fast-transmission limit problem

\[
\partial_t c - D \Delta c = r(c), \quad t \geq 0, \ z \in \Omega,
\]
\[
- \epsilon^k \cdot D \partial_n c|_{\Sigma} = 0, \quad k = 1, \ldots, n^{\Sigma}, \ t \geq 0, \ z \in \Sigma,
\]
\[
r^b(c|_{\Sigma}) = 0, \quad t \geq 0, \ z \in \Sigma,
\]
\[
c(0, \cdot) = \epsilon^0, \quad z \in \bar{\Omega}.
\]

Further assume that there is a conservation vector with strictly positive entries
\[
e \in (0, \infty)^N \cap \{\nu^a : a = 1, \ldots, m\}^\perp \cap \{\nu^{\Sigma,a} : a = 1, \ldots, m^{\Sigma}\}^\perp.
\]

Then, for every \(T_0 \in (0, T_{\text{max}}] \cap \mathbb{R}\) there is \(C = C(T_0) > 0\), also depending on the initial data \(\epsilon^0\), such that the following a-priori bounds hold true:

(a) \(L_\infty L_1\)-a-priori estimate:
\[
\sup_{t \in [0, T_0]} \|c(t, \cdot)\|_{L_1(\Omega; \mathbb{R}^N)} \leq C \|\epsilon^0\|_{L_1(\Omega; \mathbb{R}^N)};
\]

(b) \(L_1 L_\infty\)-a-priori estimate:
\[
\sup_{z \in \bar{\Omega}} \|c(\cdot, z)\|_{L_1([0, T_0); \mathbb{R}^N)} \leq C;
\]

(c) \(L_2 L_2\)-a-priori estimate:
\[
\|c\|_{L_2([0, T_0] \times \Omega; \mathbb{R}^N)} \leq C.
\]

(d) Moreover, the following entropy identity holds true:
\[
\int_\Omega c_i(t, z)(\mu^0_i + \ln c_i(t, z) - 1) \, dz \\
+ \int_0^t \int_\Omega \sum_{i=1}^N d_i \frac{|\nabla c_i(s, z)|^2}{c_i(s, z)} \, dz \, ds \\
+ \sum_{a=1}^m \int_0^t \int_\Omega \left( \sum_{i=1}^N \ln(c_i) \nu^a_i \right) \exp \left( \sum_{i=1}^N \nu^a_i \ln(c_i) - 1 \right) \, dz \, ds \\
= \int_\Omega \epsilon^0_i(z)(\mu^0_i \ln c^0_i(z) - 1) \, dz, \quad t \in [0, T_0).
\]

Proof. The a-priori bounds can be established analogously to those for standard reaction-diffusion systems, e.g., Fickian diffusion in the bulk with no-flux boundary conditions, cf. [43]. As this can be done for general reaction-diffusion-sorption systems, details will be presented in [12] and here only a sketch of the proofs will be given.

For the \(L_\infty L_1\)-estimate, one simply considers the time derivative of \(\int_\Omega c(t, z) \cdot e \, dz\), and via integration by parts and the no-flux boundary conditions \(\epsilon^k \cdot \partial_n c = 0\) on the conserved quantities, one finds that \(\int_\Omega c(t, z) \cdot e \, dz = \int_\Omega \epsilon^0(\cdot) \cdot e \, dz\) is independent of \(t \geq 0\), hence the results follow from positivity of \(c\) and \(e \in (0, \infty)^N\).

To get an \(L_1 L_\infty\)-a priori estimate, one can employ the conservation vector \(e \in (0, \infty)^N\) and consider the function \(w\) on \([0, T] \times \bar{\Omega}\) defined by \(w(t, z) = \int_0^t Dc(s, z) \cdot e \, dz\) which satisfies the differential inequality \(\partial_t w - d_{\max} \Delta w \leq d_{\max} \epsilon^0 \cdot e\) in the bulk and homogeneous no-flux boundary conditions \(-d_{\max} \partial_n w = 0\). The a priori estimate can then be derived by applying the parabolic maximum principle to \(w\).
The $L_2 L_2$-estimate can be established by considering for $T \in (0, T\text{max})$, and $d_{\text{min}} := \min_i d_i$, $d_{\text{max}} = \max_i d_i > 0$ the integral
\[
\int_0^T \int_\Omega (Dc(t, z) \cdot e)(c(t, z) \cdot e) \, dz \, dt \leq \frac{d_{\text{max}}}{d_{\text{min}}} T \| c^0 \cdot e \|_{L_{\infty}(\Omega)} \| Dc^0 \cdot e \|_{L_1(\Omega)},
\]
and using positivity of $c$.

The entropy identity can be shown as follows: By the theorem on derivatives of parameter-integrals, and as the derivative of the function $(0, \infty) \times x \mapsto x(\ln x - 1)$ is $\ln x$ for all $x \in (0, \infty)$, one finds that
\[
\frac{d}{dt} \int_\Omega \sum_{i=1}^3 c_i(\mu_i^0 + \ln(c_i) - 1) \, dz = \int_\Omega \sum_{i=1}^3 \partial_t c_i(\mu_i^0 + \ln(c_i)) \, dz = \int_\Omega \sum_{i=1}^3 d_i \Delta c_i(\mu_i^0 + \ln(c_i))
\]
\[
= - \int_\Omega \sum_{i=1}^3 d_i |\nabla c_i|^2 / c_i \, dz + \int_\Sigma \sum_{i=1}^3 \mu_i d_i \partial_n c_i \, d\sigma(z).
\]

The assertion will be established if $\sum_{i=1}^3 (\mu_i^0 + \ln(c_i)) d_i \partial_n c_i = 0$ can be proved. From the boundary conditions $e^k \cdot \partial_n(Dc) = 0$ ($k = 1, \ldots, n^\Sigma$), there are scalar functions $\eta_a : [0, T_0] \times \Sigma \rightarrow \mathbb{R}$, $a = 1, \ldots, n^\Sigma$, such that $\partial_n(Dc)|_\Sigma = \sum_a \eta_a \nu^\Sigma a$. Hence,
\[
\sum_{i=1}^N \mu_i d_i \partial_n c_i = \mu \cdot \partial_n(Dc) = \sum_a \eta_a \mu \cdot \nu^\Sigma a = \sum_a \eta_a \sum_{i=1}^N \mu_i \nu^\Sigma_i a = \sum_a \eta_a \nu^\Sigma_a = 0,
\]

since $\mu_i|_\Sigma = \mu_i^\Sigma$ at all times $t \geq 0$ and positions $z \in \Sigma$ (sorption processes in equilibrium) and $A^\Sigma_i = 0$ at all times $t \geq 0$ and all positions $z \in \Sigma$ (chemical reactions on the surface are in equilibrium). Therefore, this contribution to the sum vanishes, and the entropy identity follows by the fundamental theorem of calculus. 

\[ \square \]

3.7. Equilibria. In this subsection we compute the (spatially homogeneous) equilibria to the model problem (MP) which are compatible with the initial condition $c(0, \cdot) = c^0$. As the vectors $(1, 1, 0)^T$ and $(0, 1, 1)^T$ are conservation vectors, i.e.,
\[
\int_\Omega (c_1(t, z) + c_3(t, z)) \, dz = \int_\Omega (c_1^0 + c_3^0) \, dz, \quad \int_\Omega (c_2(t, z) + c_3(t, z)) \, dz = \int_\Omega (c_2^0 + c_3^0) \, dz
\]
are conserved quantities under the evolution of the reaction-diffusion system, we may set
\[
a = \frac{1}{|\Omega|} \int_\Omega (c_1^0 + c_3^0) \, dz \quad \text{and} \quad b = \frac{1}{|\Omega|} \int_\Omega (c_2^0 + c_3^0) \, dz.
\]

Restricting to physically relevant systems, we assume that $c^0 \geq 0$ is pointwise and componentwise non-negative, so that the solution $c \geq 0$ is non-negative as well. If $a = 0$, then $c_1^0 = c_3^0 \equiv 0$ are identically zero, and the solution to the reaction-diffusion-sorption system is clearly given by $c = (0, c_2, 0)^T$ where $c_2$ is the (unique) solution to the no-flux (homogeneous Neumann) reaction-diffusion system
\[
\begin{cases}
\partial_t c_2 - d_2 \Delta c_2 = 0 \quad \text{in } (0, \infty) \times \Omega, \\
-d_2 \partial_n c_2|_\Sigma = 0 \quad \text{on } (0, \infty) \times \Sigma, \\
c_2(0, \cdot) = c_2^0 \quad \text{on } \Omega,
\end{cases}
\]
which (for sufficiently regular initial data) exists and converges (at exponential rate) to \( c_2^\infty = b = \frac{1}{|\Omega|} \int_\Omega c_2^0 \, dz \geq 0 \), so that the corresponding equilibrium is \( c^\infty = (0, c_2^\infty, 0)^T \in \mathbb{R}_+^3 \). Similarly, the case \( b = 0 \), hence \( c_3^0 = c_3^\infty \equiv 0 \) can be handled, for which the corresponding equilibrium reads \( c^\infty = (c_1^\infty, 0, 0)^T \in \mathbb{R}_+^3 \) with \( c_1^\infty = a = \frac{1}{|\Omega|} \int_\Omega c_1^0 \, dz \).

Thus, in the following we may and will assume that \( a, b > 0 \). Note that in this case, the equilibria are spatial homogeneous and strictly positive by Proposition 3.4. In particular, for positive times \( t > 0 \), the free energy

\[
\psi(t) = \sum_{i=1}^3 \int_\Omega c_i(t) (\mu_i^0 + \ln(c_i) - 1) < \infty
\]

and thus, from the free energy dissipation relation it follows that any equilibrium state \( c^\infty \) necessarily has to satisfy

\[
\sum_{i=1}^3 \int_\Omega \frac{d}{c_i^\infty} |\nabla c_i^\infty|^2 \, dz = 0.
\]

Therefore, any equilibrium state \( c^\infty \in \mathbb{R}_+^3 \) is constant, and when \( a, b > 0 \), then \( c^\infty \in (0, \infty)^3 \). Moreover, from the conservation laws one finds that

\[
a = \frac{1}{|\Omega|} \int_\Omega (c_1^0 + c_3^0) \, dz = \frac{1}{|\Omega|} c_1^\infty + c_3^\infty, \quad \text{and} \quad b = \frac{1}{|\Omega|} \int_\Omega (c_2^0 + c_3^0) \, dz = c_2^\infty + c_3^\infty.
\]

To find the equilibrium states compatible with the initial data \( c^0 \), one thus has to solve the nonlinear problem resulting from the boundary conditions

\[
\begin{cases}
  c_1^\infty - \kappa c_2^\infty c_3^\infty = 0, \\
  \text{under the constraint } a = c_1^\infty + c_3^\infty, \quad b = c_2^\infty + c_3^\infty.
\end{cases}
\]

which, by inserting the relation for \( c_3^\infty \) into the constraints, is equivalent to

\[
\begin{align*}
  c_1^\infty (1 + \kappa c_3^\infty) &= a, \\
  c_2^\infty (1 + \kappa c_1^\infty) &= b \\
  c_3^\infty &= \kappa c_1^\infty c_2^\infty
\end{align*}
\]

The (unique, non-negative) solution of this nonlinear system is then given by

\[
\begin{align*}
  c_1^\infty &= \frac{1}{2} \sqrt{\frac{2(a + b)}{\kappa} + (b - a)^2 + \kappa^{-2} - \frac{1}{2} (\kappa^{-1} + (b - a))}, \\
  c_2^\infty &= \frac{1}{2} \sqrt{\frac{2(a + b)}{\kappa} + (b - a)^2 + \kappa^{-2} - \frac{1}{2} (\kappa^{-1} - (b - a))}, \\
  c_3^\infty &= \frac{1}{2} \sqrt{\frac{2(a + b)}{\kappa} + (b - a)^2 + \kappa^{-2} + \frac{1}{2} (\kappa^{-1} + a + b)}.
\end{align*}
\]

This is the unique equilibrium compatible with the initial data \( c^\infty \geq 0 \) such that \( a, b > 0 \). Note that as \( a \to 0 \) and/or \( b \to 0 \), the corresponding equilibria converge to the equilibria for \( a = 0 \) and/or \( b = 0 \), resp., as well.
3.8. Some comments on more general reaction-diffusion-sorption systems.
As the statements and proofs for local-in-time well-posedness and positivity of solutions have only been presented for the particular model problem (MP), some comments are in place for possible generalisations to more general reaction mechanisms.

3.8.1. Reactions in the bulk phase. Bulk chemistry can be generally allowed for in the local-in-time well-posedness and positivity results. These reactions may be handled analogously to the situation with bulk chemistry as an additional semilinear term appearing on the right hand side of the bulk diffusion equation, and which typically has enough regularity (polynomial form) to be included in the contraction mapping principle argument, cf. the standard literature on semilinear reaction-diffusion-equations; see, e.g., [43].

3.8.2. General reaction schemes for the surface chemistry. For general surface chemistry with reactions of general type \( \sum_i \alpha_i^\Sigma, a \ 
\sum_i \beta_i^\Sigma, a \ \text{⇌} \sum_i \gamma_i^\Sigma, a \), following the linearisation scheme as for the model problem (MP), one obtains a linearised version of the Dirichlet type boundary conditions \( \kappa_f^a c_{\Sigma}^{\alpha_i^\Sigma, a} = \kappa_b^a c_{\Sigma}^{\beta_i^\Sigma, a} \) as
\[
\kappa_f^a \sum_{i: \alpha_i^{\Sigma, a} > 0} \alpha_i^\Sigma, a c_{\Sigma}^{\alpha_i^\Sigma, a} - \kappa_b^a \sum_{i: \beta_i^{\Sigma, a} > 0} \beta_i^\Sigma, a c_{\Sigma}^{\beta_i^\Sigma, a} = h_a
\]
plus no-flux boundary conditions corresponding to conserved quantities. Very often, but depending on the particular structure of the reaction mechanisms, also for such more general reaction-diffusion-sorption systems, the strategy used in the proof of theorem 3.2 may be employed to establish local-in-time existence of strong solutions, provided the initial data \( c_0 \) are in \( B_{pp}^{-2/p}(\Omega; \mathbb{R}^N) \) and satisfy the compatibility conditions. However, this approach is, in general, quite tedious and essentially relies on the diagonal choice of the diffusion matrix \( D \) in the bulk, so that the reaction-diffusion equations are only coupled via the boundary conditions, and in the general case additionally over the semilinear reaction rate functions. In that case well-known maximal regularity and optimality results for the heat equation with inhomogeneous Neumann and Dirichlet boundary condition can be used again. For more general classes of diffusion in the bulk, say Fick–Onsager or Maxwell–Stefan diffusion, cross-diffusion in the bulk is allowed (and from a thermodynamic perspective even obligatory), so that for these types of systems a different approach is needed. For results in this direction, a possible approach is via the general maximal regularity and optimality results in the spirit of [24] and [25], which need to be adjusted to the particular situation here, where at the same point \( z \in \Sigma \) both Neumann and Dirichlet type boundary conditions are imposed on the system; a situation which is not covered by the theory in [24] and [25] as the definition of the principle part of the boundary symbol used there leads to a boundary symbol without Dirichlet type terms (and, hence, the Lopatinskii–Shapiro condition for the principle parts does not hold then). The abstract theory of [24] and [25], however, can be extended by slightly adjusting the notion of the principal boundary symbol; for related results, see [26], where the notion of Newton polygons is heavily used. For the model problem (MP) and a large class of more general reaction-diffusion systems, e.g., reversible versions of the free radical addition, nucleophilic substitution, the Lindemann–Hinshelwood mechanism and electrocatalysis models, the latter approach is feasible as well, as one can check the Lopatinskii–Shapiro condition at least for non-negative initial data (which serve as reference data in the
linearised system) to establish $L_p$-maximal regularity and optimality results. We abstain from giving more details here, but refer to the upcoming paper [12].

4. Summary and outlook. This manuscript covers both the modelling and the analysis of a reaction-diffusion-sorption system arising from a bulk-surface reaction-diffusion-sorption system, when considering the formal limit of fast sorption processes and fast surface chemistry, and transmission takes place in a sublayer near the surface which is very thin. On the modelling side, several fast limit models have been proposed, based on a dimensional analysis of the thermodynamic processes. It has been demonstrated that depending on the time resolution, models of different accuracy and mathematical complexity arise.

The particular case of a fast-sorption, fast-surface-chemistry limit with fast transmission between bulk and surface has been further analysed in the second part of this manuscript. As the surface chemistry takes place even faster than the transmission between bulk and surface, the boundary conditions of the resulting reaction-diffusion-system are of mixed type, in the sense that at the same time no-flux boundary conditions are imposed on the conserved quantities’ part whereas the chemical reaction equilibrium on the surface corresponds to nonlinear relations between the area surface concentrations $c^\Sigma_i$ or their chemical potentials $\mu^\Sigma_i$. Due to the sorption equilibrium condition $s^\Sigma_i(c|\Sigma, c^\Sigma) = 0$ corresponding to the fast-sorption limit, there further is a – typically nonlinear – relation between the area surface concentrations $c^\Sigma_i$ and the boundary traces of the bulk concentrations $c_i|\Sigma$. Interpreting the sorption equilibrium condition rather as an equilibrium condition for the area and bulk chemical potentials, $\mu_i|\Sigma = \mu^\Sigma_i$, one finds that the particular model for the surface chemical potentials does not play a role for the resulting limit problem, as the reaction rates (in the reaction models used here) are completely determined by the surface chemical potentials $\mu^\Sigma_i$, so in the limit case by the traces of the bulk chemical potentials $\mu_i|\Sigma$. The particular structure of the conservation vectors $e^a$ for the surface chemical reactions being orthogonal to the stoichiometric vectors $\nu^\Sigma \cdot a$ of the surface chemical reactions, can then be used to derive $L_p$-maximal regularity for a suitable linearisation of the semilinear fast limit model. From there (local-in-time) existence and uniqueness of strong solutions, (first, rough) blow-up criteria and a-priori bounds have been derived.

REFERENCES

[1] P. Acquistapace and B. Terreni, Fully nonlinear parabolic systems, Recent Advances in Nonlinear Elliptic and Parabolic Problems (Nancy, 1988), Pitman Res. Notes Math. Ser. Longman Sci. Tech., Harlow, 208 (1989), 97–111.
[2] H. Amann, Dual semigroups and second order linear elliptic boundary value problems, Israel J. Math., 45 (1983), 225–254.
[3] H. Amann, Global existence for semilinear parabolic systems, J. Reine Angew. Math., 360 (1985), 47–83.
[4] H. Amann, Dynamic existence theory of semilinear parabolic systems, J. Reine Angew. Math., 360 (1985), 47–83.
[5] H. Amann, Dynamic theory of quasilinear parabolic equations. I. Abstract evolution equations, Nonlinear Anal., 12 (1988), 895–919.
[6] H. Amann, Parabolic evolution equations and nonlinear boundary conditions, J. Differential Equations, 72 (1988), 201–269.
[7] H. Amann, Dynamic theory of quasilinear parabolic systems. III. Global existence, Math. Z., 202 (1989), 219–250.
[8] H. Amann, Dynamic theory of quasilinear parabolic equations. II. Reaction-diffusion systems, Differential Integral Equations, 3 (1990), 13–75.
[8] H. Amann, Nonhomogeneous linear and quasilinear elliptic and parabolic boundary value problems, in Function Spaces, Differential Operators and Nonlinear Analysis (Friedrichska, 1992), Teubner-Texte Math. Teubner, Stuttgart, 133 (1993), 9–126.
[9] H. Amann, Linear and Quasilinear Parabolic Problems. Vol. I. Abstract Linear Theory, Monographs in Mathematics, 89. Birkhäuser Boston, Inc., Boston, MA, 1995.
[10] H. Amann, Linear and Quasilinear Parabolic Problems. Vol. II. Function Spaces, Monographs in Mathematics, 106. Birkhäuser/Springer, Cham, 2019.
[11] B. Augner and D. Bothe, A thermodynamically consistent model for bulk-surface systems with sorption and surface chemistry, in preparation.
[12] B. Augner and D. Bothe, Analysis of some heterogeneous catalysis models with fast sorption and fast surface chemistry, submitted (2020), https://arxiv.org/abs/2006.12098.
[13] E. Berkson and T. A. Gillespie, Spectral decompositions and harmonic analysis on UMD spaces, Studia Math., 112 (1994), 13–49.
[14] D. Bothe, The instantaneous limit of a reaction-diffusion system, in Evolution Equations and their Applications in Physical and Life Sciences (Bad Herrenalb, 1998), Lecture Notes in Pure and Appl. Math., Dekker, New York, 215 (2001), 215–224.
[15] D. Bothe, On the Maxwell-Stefan approach to multicomponent diffusion, in Parabolic problems, Progr. Nonlinear Differential Equations Appl., Birkhäuser/Springer Basel AG, Basel, 80 (2011), 81–93.
[16] D. Bothe and W. Dreyer, Continuum thermodynamics of chemically reacting fluid mixtures, Acta Mech., 226 (2015), 1757–1805.
[17] D. Bothe, M. Köhne, S. Maier and J. Saal, Global strong solutions for a class of heterogeneous catalysis models, J. Math. Anal. Appl., 445 (2017), 677–709.
[18] D. Bothe and M. Pierre, Quasi-steady-state approximation for a reaction-diffusion system with fast intermediate, J. Math. Anal. Appl., 368 (2010), 120–132.
[19] D. Bothe and M. Pierre, The instantaneous limit for reaction-diffusion systems with a fast irreversible reaction, Discrete Contin. Dyn. Syst. Ser. S, 5 (2012), 49–59.
[20] D. Bothe and G. Rolland, Global existence for a class of reaction-diffusion systems with mass action kinetics and concentration-dependent diffusivities, Acta Appl. Math., 139 (2015), 25–57.
[21] H. Brenner, Is the tracer velocity of a fluid continuum equal to its mass velocity?, Phys. Rev. E, 70 (2004), 061201.
[22] J. A. Cañizo, L. Desvillettes and K. Fellner, Improved duality estimates and applications to reaction-diffusion equations, Comm. Partial Differential Equations, 39 (2014), 1185–1204.
[23] P. Clément, B. de Pagter, F. A. Sukochev and H. Witvliet, Schauder decomposition and multiplier theorems, Studia Math., 138 (2000), 135–163.
[24] R. Denk, M. Hieber and J. Prüss, R-boundedness, Fourier multipliers and problems of elliptic and parabolic type, Mem. Amer. Math. Soc., 166 (2003), viii+114 pp.
[25] R. Denk, M. Hieber and J. Prüss, Optimal Lp-Lq estimates for parabolic boundary value problems with inhomogeneous data, Math. Z., 257 (2007), 193–224.
[26] R. Denk and M. Kain, General Parabolic Mixed Order Systems in Lp and Applications, Operator Theory: Advances and Applications, 239. Birkhäuser/Springer, Cham, 2013.
[27] R. Denk, J. Prüss and R. Zacher, Maximal Lp-regularity of parabolic problems with boundary dynamics of relaxation type, J. Funct. Anal., 255 (2008), 3149–3187.
[28] L. Desvillettes and K. Fellner, Exponential decay toward equilibrium via entropy methods for reaction-diffusion equations, J. Math. Anal. Appl., 319 (2006), 157–176.
[29] L. Desvillettes, K. Fellner, M. Pierre and J. Vovelle, Global existence for quadratic systems of reaction-diffusion, Adv. Nonlinear Stud., 7 (2007), 491–511.
[30] L. Desvillettes and K. Fellner, Entropy methods for reaction-diffusion equations: Slowly growing a-priori bounds, Rev. Mat. Iberoam., 24 (2008), 407–431.
[31] L. Desvillettes, K. Fellner and B. Q. Tang, Trend to equilibrium for reaction-diffusion systems arising from complex balanced chemical reaction networks, SIAM J. Math. Anal., 49 (2017), 2666–2709.
[32] P.-E. Druet and A. Jüngel, Analysis of cross-diffusion systems for fluid mixtures driven by a pressure gradient, SIAM J. Math. Anal., 52 (2020), 2179–2197.
[33] J. B. Duncan and H. L. Toor, An experimental study of three component gas diffusion, A. I. Ch. E. Journal, 8 (1962), 38–41.
[34] R. Haase, Thermodynamik Irreversibler Prozesse, Fortschritte der physikalischen Chemie, 8, Steinkopff, Darmstadt, 1963.
[35] D. Henry, *Geometric Theory of Semilinear Parabolic Equations*, Lecture Notes in Math., 840, Springer-Verlag, 1981.

[36] M. Herberg, M. Meyries, J. Prüss and M. Wilke, Reaction-diffusion systems of Maxwell-Stefan type with reversible mass-action kinetics, *Nonlinear Anal.*, 159 (2017), 264–284.

[37] N. J. Kalton and L. Weis, The $H^\infty$-calculus and sums of closed operators, *Math. Ann.*, 321 (2001), 319–345.

[38] O. A. Ladyzenskaya, V. A. Solonnikov and N. N. Ural’ceva, *Linear and Quasi-linear Equations of Parabolic Type*, (Russian) Translated from the Russian by S. Smith. Translations of Mathematical Monographs, Vol. 23 American Mathematical Society, Providence, R.I. 1968.

[39] A. Lunardi, *Analytic Semigroups and Optimal Regularity in Parabolic Problems*, Progress in Nonlinear Differential Equations and their Applications, 16. Birkhäuser Verlag, Basel, 1995.

[40] A. Lunardi, *Interpolation Theory*, 3rd Edition, Appunti. Scuola Normale Superiore di Pisa (Nuova Serie), 16, Edizioni della Normale, Pisa, 2018.

[41] R. H. Martin and M. Pierre, Nonlinear reaction-diffusion systems, in *Nonlinear Equations in the Applied Sciences*, (eds. W.F. Ames and C. Rogers), Math. Sci. Engrg., Academic Press, Boston, MA, 185 (1992), 363–398.

[42] M. Pierre, Weak solutions and supersolutions in $L^1$ for reaction-diffusion systems, *J. Evol. Equ.*, 3 (2003), 153–168.

[43] M. Pierre, Global existence in reaction-diffusion systems with control of mass: A survey, *Milan J. Math.*, 78 (2010), 417–455.

[44] M. Pierre and D. Schmitt, Blow up in reaction-diffusion systems with dissipation of mass, *SIAM J. Math. Anal.*, 28 (1997), 259–269.

[45] M. H. Protter and H. F. Weinberger, *Maximum Principles in Differential Equations*, Prentice-Hall Inc., Englewood Cliffs, N. J., 1967.

[46] F. Rothe, *Global Solutions of Reaction-Diffusion Systems*, Lecture Notes in Mathematics, 1072, Springer, Berlin, 1984.

[47] R. Schnaubelt, Stable and unstable manifolds for quasilinear parabolic problems with fully nonlinear dynamical boundary conditions, *Advances in Differential Equations*, 22 (2017), 541–592.

[48] O. Souček, V. Orava, J. Málek and D. Bothe, A continuum model of heterogeneous catalysis: Thermodynamic framework for multicomponent bulk and surface phenomena coupled by sorption, *Int. J. Eng. Sci.*, 138 (2019), 82–117.

[49] B. Terreni, Hölder regularity results for nonhomogeneous parabolic initial-boundary value linear problems, in *Semigroup Theory and Applications (Trondheim, 1987)*, Lecture Notes in Pure and Appl. Math. Dekker, New York, 116 (1989), 387–401.

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*E-mail address: augner@mma.tu-darmstadt.de*

*E-mail address: bothe@mma.tu-darmstadt.de*