Mixed Finite Element Methods for Addressing Multi-Species Diffusion Using the Maxwell-Stefan Equations

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Abstract

The Maxwell-Stefan equations are a system of nonlinear partial differential equations that describe the diffusion of multiple chemical species in a container. These equations are of particular interest for their applications to biology and chemical engineering. The nonlinearity and coupled nature of the equations involving many variables rule out analytical solutions, so numerical methods are often used. In the literature the system is inverted to write fluxes as functions of the species gradient before any numerical method is applied. In this paper it is shown that employing a mixed finite element method makes the inversion unnecessary, allowing the numerical solution of Maxwell-Stefan equations in their primitive form. A mixed variational formulation is derived in the general n-ary case. A priori error estimates between the finite element and exact solutions are obtained. The order of convergence of the method is then verified and compared with standard methods using a manufactured solution. Finally, the solution is computed for a test case from the literature involving the diffusion of three species and compared to solutions from other methods.

Keywords: Maxwell-Stefan, mixed finite element, multi-species diffusion

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1. Introduction

The Maxwell-Stefan equations describe the process of diffusion in a mixture of multiple chemical species. This model was independently derived in [1] and [2]. Aside from a firm experimental confirmation [3], this model has several applications to biology and chemical engineering. A detailed discussion of the physics behind the Maxwell-Stefan equations can be found in [4] or [5]. These equations form a degenerate system linking the species concentration and fluxes, where each concentration gradient is expressed as a combination of all the fluxes.

The usual method for finding a numerical solution is to remove the degeneracy, invert the system and apply a finite element method to compute only the species concentrations. For instance, in [6] a model for bone tissue growth using coupled Navier-Stokes and Maxwell-Stefan equations is described. The authors invert the Maxwell-Stefan equations to express the fluxes in terms of gradients of mass fractions before applying a finite element method using the software Femlab. In [7] a benchmark for diffusion and fluid flow is introduced. The model used relies on an inversion of the Maxwell-Stefan equations before applying a finite element method to find the solution. A model of water transport in a fuel cell is described in [8] using Maxwell-Stefan equations and concentrated solution theory. The flux of water at the membrane is determined using concentrated solution theory. The fluxes are expressed in terms of the mass fractions before applying a finite element method, except on the boundary where normal fluxes are used as boundary conditions. The stability of the finite element method for Maxwell-Stefan equations is considered in [9]. The system is inverted so that the flux is written explicitly in terms of the mass fractions before any finite element method is applied. A finite volume approach is applied in [10] where the flux is written in a discretized form using what the authors refer to as a “coupled exponential scheme”.

Less often a finite difference scheme is used to solve numerically the Maxwell-Stefan equations. In [11] a finite difference scheme expressed in mole fractions and velocities is used to approximate the gradients of the mole fractions. The molar flux is written in terms of the velocities and mole fractions and solutions are found using a 4th order Runge-Kutta scheme. A 1D problem is considered in [12] to study the phenomena of uphill diffusion. The Maxwell-Stefan equations are solved using a finite difference discretization. The numerical method is shown to be second order and a condition for $L^\infty$-stability is found. Another 1D problem is studied in [13], where a shoot-
ing method is used to solve the boundary value problem and a Runge-Kutta method is used to solve the associated ordinary differential equations.

Recently work has been done looking at the mathematical properties of Maxwell-Stefan equations \[12, 14\]. In \[12\], it is shown that if the initial solutions \(\xi_{i}^{in}\) are nonnegative functions in \(L^{\infty}(\Omega)\) then the Maxwell-Stefan equations admit an unique smooth solution with molar fractions \(\xi_{i}\) remaining nonnegative for all time \(t > 0\). It has been shown in \[14\] that the homogeneous system is well-posed for a solution that is local in time. Additionally the same paper has shown that the mole fractions \(\xi_{i}\) are non-negative for the inhomogeneous case, under certain conditions on the reaction rates. A main piece of the argument in both proofs is that the system is invertible for each \(J_{i}\) as a function of \(\nabla \xi_{j}\).

There has been, until now, no work done on the Maxwell-Stefan equations in the context of mixed variational formulations. This is true both for the theoretical analysis of the model and its numerical solution. This is surprising as these equations naturally state with primal and dual variables as is commonly seen in mixed formulations. The goal of the current paper is to propose a mixed variational formulation for Maxwell-Stefan equations and to see how the theory for mixed finite element methods applies to these equations after an appropriate linearization. As will be seen, two main advantages will result from such mixed formulation of the Maxwell-Stefan equations: the system only shows mild (quadratic) nonlinearity, and both the mole fractions and molar fluxes will be approximated with an equal order of accuracy. These two features are simply not true or possible with the standard methods advocated in the literature and requiring the expression of \(J_{i}\) as a function of all \(\nabla \xi_{j}\).

The paper is organized in the following way. In section 2 the Maxwell-Stefan model is briefly derived with accompanying boundary conditions. In section 3, standard finite element methods are presented and discussed as they will be compared to our methods. In section 4 a mixed variational formulation is derived for n-ary diffusion problems. Section 5 analyzes the well-posedness of Maxwell-Stefan equations applied to ternary diffusion. In Section 6 the mixed finite element approximation is established as well as error estimates. In Section 7 the error estimates are verified through numerical tests using a test case with a known analytic solution. In this section another test case is conducted and the solution is compared to results from the literature.
2. The Maxwell-Stefan equations

Physically the system represents a mixture of \( n \) ideal gases, where each species \( i \) has a mole fraction of \( \xi_i \) and a flux of \( J_i \), in moles per unit area per unit of time. If the mixture reaches steady state, the divergence of the flux will be equal to some reaction rate \( r_i \). This leads to the following equations for \( i = 1, 2, ..., n \):

\[
\nabla \cdot J_i = r_i. \tag{1}
\]

The motion of the gases will cause the particles of each species to be dragged by the particles of the other species in the mixture. This drag force is balanced by the partial pressure gradients of the species in the mixture. This leads to the following expression for \( i = 1, 2, ..., n \):

\[
-\nabla \xi_i = \frac{1}{c_{\text{tot}}} \sum_{j=1}^{n} \frac{\xi_j J_i - \xi_i J_j}{D_{ij}}, \tag{2}
\]

where \( D_{ij} \) is the binary diffusion coefficient between species \( i \) and species \( j \), and \( c_{\text{tot}} > 0 \) is the total concentration of the mixture. The coefficients \( D_{ij} \) and \( D_{ji} \) are taken to be equal.

Consider a domain \( \Omega \subset \mathbb{R}^d \), such that the boundary \( \Gamma \) is divided into two components, \( \Gamma_D \) and \( \Gamma_N \). These components satisfy: \( \Gamma_D \cap \Gamma_N = \emptyset \). On the boundary \( \Gamma_D \), the mole fraction \( \xi_i \) is equal to \( f_i \). On \( \Gamma_N \), the normal flux of species \( i \), \( J_i \cdot \nu \), is taken to be \( g_i \). Since the variable \( \xi_i \) represents mole fractions, at any point in the domain the following condition holds:

\[
\sum_{i=1}^{n} \xi_i = 1. \tag{3}
\]

To close the system we will make use of the following fact [12, 14]:

\[
\sum_{i=1}^{n} J_i = 0. \tag{4}
\]

We will use the following notations:

\[
\xi = (\xi_1, \xi_2, ..., \xi_n),
J = (J_1, J_2, ..., J_n).
\]
The Maxwell-Stefan problem for n-ary diffusion becomes: Find \((J, \xi)\) such that equations (1)-(4) are satisfied in \(\Omega\) for \(i = 1, 2, ..., n\) with the following boundary conditions:

\[
\xi_i = f_i \quad \text{on} \quad \Gamma_D, \tag{5}
\]
\[
J_i \cdot \nu = g_i \quad \text{on} \quad \Gamma_N. \tag{6}
\]

3. Standard finite element formulation of Maxwell-Stefan equations

For the sake of completeness, finite element methods commonly used to solve Maxwell-Stefan equations are presented and discussed here. By taking equation (2) and using equations (3) and (4), the \(n\)-species system is reduced to the following system with \(n-1\) species:

\[
-\nabla \xi_i = \sum_{j=1}^{n-1} A_{ij} J_j,
\]
for \(i = 1, 2, \ldots, n-1\). The matrix \(A\) is derived by unpleasant calculations. For instance, for a three-species system this gives:

\[
A = \begin{pmatrix}
\tilde{\alpha}_1 & \tilde{\alpha}_2 \\
\tilde{\beta}_1 & \tilde{\beta}_2
\end{pmatrix},
\]
where the terms in the matrix are defined below by equations (16)-(19).

The fluxes can be expressed in terms of the mole fractions and their gradients by inverting the equation above to give:

\[
J_i = -\sum_{j=1}^{n-1} A_{ij}^{-1} \nabla \xi_j, \tag{7}
\]
for \(i = 1, 2, \ldots, n-1\).

By taking the divergence on both sides and applying equation (1), we obtain the following equations for \(i = 1, 2, \ldots, n-1\):

\[
-\nabla \cdot \left( \sum_{j=1}^{n-1} A_{ij}^{-1} \nabla \xi_j \right) = r_i.
\]
The variational formulation is obtained by multiplying the above equation by a test function \( \phi_i \) and integrating by parts to remove the divergence term. For a Dirichlet problem this yields the following variational formulation: Find \( \xi \in (H^1(\Omega))^2 \) with \( \xi_i = f_i \) on \( \Gamma \) such that:

\[
\int_{\Omega} \left( \sum_{j=1}^{n-1} A_{ij}^{-1} \nabla \xi_j \right) \cdot \nabla \phi_i \, dx = \int_{\Omega} r_i \phi_i \, dx, \tag{8}
\]

for all \( \phi_i \in H^1_0(\Omega) \) and \( i = 1, 2, \ldots, n - 1 \). The finite element approximation is taken as the usual space of continuous piecewise polynomials \( P^k \) of degree \( k \), for \( k \geq 1 \). These finite element methods will be referred to as “Standard \( P^k \).

The matrix \( A \) being dependent on the mole fractions, a fixed point method is required to solve the nonlinearity, such as Newton-Raphson method. A first drawback of Standard \( P^k \) methods comes from the fact that the matrix \( A^{-1} \) that appears in (8) involves the mole fractions in a non-trivial nonlinear way. This makes the application of Newton-Raphson method tedious and potentially leads to a lack of convergence of the method. To avoid these issues, we applied a simple fixed point method (Picard method): Given initial guesses \( \tilde{\xi}_{h,i} \), \( i = 1, 2, \ldots, n - 1 \), the matrix \( A^{-1} \) is computed using these \( \tilde{\xi}_{h,i} \) and problem (8) is solved for \( \xi_{h,i} \), \( i = 1, 2, \ldots, n - 1 \). A new guess is then defined using the relaxation formula \( \tilde{\xi}_{h,i} := \sigma \xi_{h,i} + (1 - \sigma)\tilde{\xi}_{h,i} \) for \( \sigma \in [0, 1] \) and the loop is repeated until convergence.

A second drawback of Standard \( P^k \) methods is that fluxes \( J_i \) are not readily available while they are often needed. They can be recovered from \( \xi \) using equation (7). This leads to a rational function for each component of \( J_i \) on any element of the mesh, which rational function can be re-interpolated by a polynomial in \( P^{2k} \) at the element level. Re-interpolation with \( P^{2k} \) polynomials yielded the lowest \( L^2 \) error on the fluxes for the numerical tests presented below, still accuracy on the fluxes is usually one order lower than on mole fractions for Standard \( P^k \) methods.

4. Mixed variational formulation of Maxwell-Stefan equations

To define the functional spaces used in this section, we will need the following normal trace operator:

\[
\gamma_{\nu,\Gamma_N}(q) = q \cdot \nu|_{\Gamma_N}, \quad \forall q \in C^\infty(\overline{\Omega}),
\]
where $\nu$ is the outward pointing normal vector. This operator is extended by density to the weaker space given below.

In this section we use the following spaces:

$$V = (L^2(\Omega))^{n-1}$$ equipped with the norm $|| \cdot ||_V = || \cdot ||_0$;

$$Q = (H(div; \Omega))^{n-1}$$ and

$$Q_g = \{ q \in (H(div; \Omega))^{n-1} | \gamma_{\nu, \Gamma_N}(q_i) = g_i \text{ on } \Gamma_N \},$$

both equipped with the norm $|| \cdot ||_Q = || \cdot ||_{H(div; \Omega)}$.

The space $Q_0$ is the particular case when $g_i = 0$ on $\Gamma_N$ in $Q_g$. To define the weak formulation we reduce the system to $n-1$ species by using relations (3) and (4). Multiplying the resulting system of equations by test functions and applying integration by parts yields the following weak formulation: Find $(J, \xi) \in Q_g \times V$ such that,

$$\int_\Omega \left\{ \frac{J_i \cdot q_i}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_i J_j \cdot q_i - \xi_j J_i \cdot q_i) \right\} \, dx$$

$$- \int_\Omega \xi_i \nabla \cdot q_i \, dx = - < q_i \cdot \nu, f_i > |_{\Gamma_D},$$

$$\int_\Omega v_i \nabla \cdot J_i \, dx = \int_\Omega r_i v_i \, dx,$$

for $i = 1, 2, ..., n-1$ and $\forall q = (q_1, q_2, ..., q_{n-1}) \in Q_0$, $\forall v = (v_1, v_2, ..., v_{n-1}) \in V$, where $< q_i \cdot \nu, f_i >_{\Gamma_D}$ is a duality product between $H^{-1/2}(\Gamma)$ and $H^{1/2}(\Gamma)$ restricted to functions that are null on $\Gamma_N$. In all the paper, the coefficients $\alpha_{ij}$ are defined as

$$\alpha_{ij} = 1/D_{in} - 1/D_{ij}.$$ 

It is useful to know which conditions ensure that a solution to the variational formulation is also a solution to the Maxwell-Stefan equations. We will make use of $D(\Omega)$, the space of infinitely differentiable functions with compact support on $\Omega$. Now let $(J, \xi) \in Q_g \times V$ be a solution to the above mixed variational formulation. By rearranging (10) we get the following equality for all $v_i \in L^2(\Omega)$:

$$\int_\Omega (\nabla \cdot J_i - r_i) v_i \, dx = 0.$$
Since \( J_i \in H(\text{div}; \Omega) \), we know that \( \nabla \cdot J_i \) is an \( L^2 \)-function. By taking \( v_i \in D(\Omega) \subset L^2(\Omega) \) we recover \( \nabla \cdot J_i = r_i \) in the sense of distributions and since both sides of this equality are in \( L^2(\Omega) \), the equation is true almost everywhere on \( \Omega \).

To recover the rest of the Maxwell-Stefan problem we consider (9). If we assume that \( \xi_i \in H^1(\Omega) \) then we can apply integration by parts to the terms \( \xi_i \nabla \cdot q_i \) and get:

\[
0 = \int_\Omega \left( \frac{J_i}{c_{\text{tot}}D_m} + \sum_{j=1}^{n-1} \alpha_{ij} (\xi_i J_j - \xi_j J_i) + \nabla \xi_i \cdot q_i \right) \cdot q_i \, dx
\]

\[
- < q_i \cdot \nu, \xi_i >_{\Gamma_N} + < q_i \cdot \nu, f_i - \xi_i >_{\Gamma_D}
\]

The above equation is true for all \( q_i \in H(\text{div}; \Omega) \), so take \( q_i \in (D(\Omega))^d \subset H(\text{div}; \Omega) \). Since \( q_i \) vanishes on \( \Gamma \) we recover equation (2) in the sense of distributions. To recover the boundary conditions, take \( q_i \) equal to zero on \( \Gamma_N \). This choice of \( q_i \) is possible due to the surjectivity of the operator \( \gamma_{\nu, \Gamma_N} \). For this choice of \( q_i \) we obtain that:

\[
< q_i \cdot \nu, f_i - \xi_i >_{\Gamma_D} = 0 \quad \forall q \cdot \nu \in H^{-1/2}(\Gamma_D),
\]

which implies that \( f_i = \xi_i \) in \( H^{1/2}(\Gamma_D) \). Since \( H^{1/2}(\Gamma_D) \subset L^2(\Gamma_D) \), we get that \( f_i = \xi_i \) almost everywhere on \( \Gamma_D \). The boundary condition on the normal flux of \( J \) is satisfied in \( H^{-1/2}(\Gamma_N) \) since it \( J \in Q_g \).

So a solution to the mixed variational formulation with \( \xi \in (H^1(\Omega))^{n-1} \), will also be a solution to the Maxwell-Stefan problem.

5. Existence and uniqueness for the linearized ternary Maxwell-Stefan equations

In this section the Maxwell-Stefan problem is analyzed using the theory of mixed variational formulations, often referred to as abstract saddle point problems. This theory will be briefly reviewed here, based on [15, Ch. II]. Following this review, the general theory will be applied to the case of ternary diffusion. To study the well-posedness of the weak formulation we shall linearize the problem by taking the variable \( \xi_i \) to be a known non-negative function \( \xi_i \) whenever it is multiplied by a flux \( J_j \).

Take \( V \) and \( Q \) to be Hilbert spaces with inner products \( (\cdot, \cdot)_V \) and \( (\cdot, \cdot)_Q \), respectively, and their associated norms defined as \( \| \cdot \|_V \) and \( \| \cdot \|_Q \). Define
two bounded bilinear forms $a(\cdot,\cdot): Q \times Q \to \mathbb{R}$ and $b(\cdot,\cdot): Q \times V \to \mathbb{R}$. The abstract saddle point problem is stated as follows: Given $f \in Q^*$ and $r \in V^*$ find $(J, \xi) \in Q \times V$ such that:

\begin{equation}
\begin{aligned}
    a(J, q) + b(q, \xi) &= \langle f, q \rangle_{Q^* \times Q} \quad \forall q \in Q, \\
    b(J, v) &= \langle r, v \rangle_{V^* \times V}, \quad \forall v \in V,
\end{aligned}
\end{equation}

where $V^*$ and $Q^*$ are taken to be the dual spaces of $V$ and $Q$ with $\langle \cdot, \cdot \rangle$ denoting duality products. The saddle point formulation can be given in an equivalent operator form by defining operators $A: Q \to Q^*, B: Q \to V^*$, and $B^*: V \to Q^*$ such that:

\begin{equation}
\begin{aligned}
    \langle Ap, q \rangle_{Q^* \times Q} &= a(p, q) \quad \forall p, q \in Q, \\
    \langle Bq, v \rangle_{V^* \times V} &= \langle q, B^*v \rangle_{Q^* \times Q} = b(q, v) \quad \forall v \in V, \forall q \in Q,
\end{aligned}
\end{equation}

where $B^*$ is the adjoint of $B$. This yields the following saddle point problem:

$$AJ + B^*\xi = f \quad \text{in} \quad Q^*,
$$

$$BJ = r \quad \text{in} \quad V^*.$$

To ensure the existence of a solution to the above saddle point problem, we make use of the following theorem [15, p.42], where in our case $q$ is the primal variable and $v$ the dual variable:

**Theorem 1.** Let $V$ and $Q$ be Hilbert spaces and $a(\cdot,\cdot)$ and $b(\cdot,\cdot)$ be bounded bilinear forms with associated operators $A$ and $B$, such that the following conditions hold:

- The bilinear form $a(\cdot,\cdot)$ satisfies the coercivity condition over $\text{Ker}(B)$:
  \begin{equation}
  a(p, p) \geq \lambda \|p\|_Q^2 > 0, \quad \forall p \in \text{Ker}(B). \tag{14}
  \end{equation}

- The bilinear form $b(\cdot,\cdot)$ satisfies the inf-sup condition:
  \begin{equation}
  \inf_{v \in V \setminus \text{Ker}(B^*)} \sup_{q \in Q} \frac{b(q, v)}{\|q\|_Q \|v\|_V} \geq \mu > 0 \tag{15}
  \end{equation}

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Then for any \( f \in V^* \) and \( r \in \text{Im}(B) \), the saddle point problem (12)-(13) admits a solution \((J, \xi) \in Q \times V\) where \( J \in Q \) is uniquely determined and \( \xi \in V \) is unique up to an element of \( \text{Ker}(B^*) \).

For the Maxwell-Stefan equations the case of ternary diffusion will be considered. Since there are only three binary diffusion coefficients, it is always possible to ensure that \( D_{12} \) is the largest by relabeling the three species. Define the following quantities:

\[
\tilde{\alpha}_1 = \frac{1}{D_{13}} - \alpha_{12} \xi_2, \\
\tilde{\alpha}_2 = \alpha_{12} \xi_1, \\
\tilde{\beta}_1 = \alpha_{21} \xi_2, \\
\tilde{\beta}_2 = \frac{1}{D_{23}} - \alpha_{21} \xi_1,
\]

where \( \xi_1 \) and \( \xi_2 \) are assumed to be known non-negative mole fractions as required for the linearization. The mole fractions \( \xi_1 \) and \( \xi_2 \) will be taken in \( L^\infty(\Omega) \) to ensure the continuity of the bilinear form \( a(\cdot, \cdot) \).

Define two bilinear forms \( a(\cdot, \cdot) : Q \times Q_0 \rightarrow \mathbb{R} \) and \( b(\cdot, \cdot) : Q \times V \rightarrow \mathbb{R} \):

\[
a(p, q) = \frac{1}{c_{\text{tot}}} \int_{\Omega} \left( \tilde{\alpha}_1 p_1 \cdot q_1 + \tilde{\alpha}_2 p_2 \cdot q_1 \right) dx + \frac{1}{c_{\text{tot}}} \int_{\Omega} \left( \tilde{\beta}_1 p_1 \cdot q_2 + \tilde{\beta}_2 p_2 \cdot q_2 \right) dx,
\]

\[
b(q, v) = -\int_{\Omega} (v_1 \nabla \cdot q_1 + v_2 \nabla \cdot q_2) dx.
\]

Using the bilinear forms the problem can be restated as follows: Find \((J, \xi) \in Q_0 \times V\) such that

\[
a(J, q) + b(q, \xi) = -< q \cdot \nu, f >_{\Gamma_D}, \quad \forall q \in Q_0, \quad (22)
\]

\[
b(J, v) = -\int_{\Omega} r \cdot v \; dx, \quad \forall v \in V, \quad (23)
\]

where \( r = (r_1, r_2) \in V \) and \( f = (f_1, f_2) \in H^{1/2}(\Gamma_D) \) corresponds to the Dirichlet boundary conditions on \( \xi \).
Remark 1. In the case where \( J \notin Q_0 \) the problem can be reformulated as above through a continuous lifting. In order to apply Theorem 1, the unknowns \( J \) and \( \xi \) must lie in Hilbert spaces. This is a problem since \( Q_g \) is not a Hilbert Space. Fortunately this can be resolved by letting \( J = J_0 + J_g \) where \( J_0 \in Q_0 \) and \( J_g \in Q_g \). This lifting is possible since \( \gamma_{\nu, \Gamma_N} \) is surjective on \( H^{-1/2}(\Omega) \). So for any \( g \) there will exist a \( J_g \), not necessarily unique, lifting \( g \). This will result in different right hand sides for equations (22) and (23) but the proof remains the same.

Now to obtain the existence of a solution to this linearized problem we need to prove that the bilinear forms \( a(\cdot, \cdot) \) and \( b(\cdot, \cdot) \) satisfy the hypothesis of Theorem 1. To start, consider the following lemma:

\textbf{Lemma 1.} If \( \min(\frac{1}{D_{12}}, \frac{1}{D_{13}}, \frac{1}{D_{23}}) = \frac{1}{D_{12}} > 0 \), then we have that \( \tilde{\alpha}_1 - \tilde{\alpha}_2 \geq \frac{1}{D_{12}} \) and \( \tilde{\beta}_2 - \tilde{\beta}_1 \geq \frac{1}{D_{12}} \).

\textbf{Proof.} We first prove that \( \tilde{\alpha}_1 - \tilde{\alpha}_2 \geq \frac{1}{D_{12}} \).

\[
\tilde{\alpha}_1 - \tilde{\alpha}_2 = \frac{1}{D_{13}} - \left( \frac{1}{D_{13}} - \frac{1}{D_{12}} \right) \xi_1 - \left( \frac{1}{D_{13}} - \frac{1}{D_{12}} \right) \xi_2 \\
= \frac{1 - \xi_1}{D_{13}} + \frac{\xi_1}{D_{12}} - \frac{\xi_2}{D_{13}} - \frac{\xi_2}{D_{12}} \\
= \frac{1 - \xi_1 - \xi_2}{D_{13}} + \frac{\xi_1 + \xi_2}{D_{12}} \\
\geq \frac{1 - \xi_1 - \xi_2}{D_{12}} + \frac{\xi_1 + \xi_2}{D_{12}} \\
= \frac{1}{D_{12}}
\]

We have used the fact that the \( \xi_i \)'s add up to one and that the binary diffusion coefficient \( D_{12} \) is the largest.

To prove the other inequality, one proceeds in a similar fashion. \( \square \)

We now consider the coercivity of \( a(\cdot, \cdot) \) with the following proposition:

\textbf{Proposition 1.} If the binary diffusion coefficients satisfy \( 3D_{23} > D_{12}, \) \( 3D_{13} > D_{12}, \) and \( c_{\text{tot}} \in C(\Omega) \) then the bilinear form \( a(\cdot, \cdot) \) is coercive over \( Q \).
Proof. We rewrite the bilinear form in the following way:

\[
a(p, q) = \int_{\Omega} \frac{1}{c_{\text{tot}}^2} \sum_{i=1}^{2} \left( q_{1i}^1, q_{2i}^1 \right) \left( \tilde{\alpha}_1, \tilde{\beta}_1 \right) \left( p_{1i}^i, p_{2i}^i \right) dx
\]

Since \( c_{\text{tot}} > 0 \) in \( \overline{\Omega} \), there exist real numbers \( c_{\text{min}} \) and \( c_{\text{max}} \) such that \( 0 < c_{\text{min}} \leq c_{\text{tot}} \leq c_{\text{max}} \) everywhere in \( \Omega \). So when bounding the bilinear form from above or below, we can use \( c_{\text{min}} \) or \( c_{\text{max}} \) and ignore \( c_{\text{tot}} \).

The bilinear form is coercive if and only if the symmetric part of the matrix is positive definite with the smallest eigenvalue uniformly bounded away from 0 for all \( \tilde{\xi}_i \). So to prove the coercivity we will consider

\[
A_{\text{sym}} = \begin{pmatrix}
\tilde{\alpha}_1 & \frac{\tilde{\alpha}_2 + \tilde{\beta}_1}{\tilde{\beta}_2} \\
\frac{\tilde{\alpha}_2 + \tilde{\beta}_1}{\tilde{\beta}_2} & \tilde{\beta}_2
\end{pmatrix}
\]

and apply the Gershgorin circle theorem to find lower bounds on the eigenvalues of \( A_{\text{sym}} \). For the first row, this gives:

\[
2\tilde{\alpha}_1 - (\tilde{\alpha}_2 + \tilde{\beta}_1) \geq 2\tilde{\alpha}_1 - (\tilde{\alpha}_1 - \frac{1}{D_{12}} + \tilde{\beta}_1)
\]

\[
= \frac{1}{D_{13}} - \alpha_{12} \tilde{\xi}_2 - \alpha_{21} \tilde{\xi}_2 + \frac{1}{D_{12}}
\]

\[
= \frac{1}{D_{13}} - \left( \frac{1}{D_{13}} - \frac{1}{D_{12}} \right) \tilde{\xi}_2 - \left( \frac{1}{D_{23}} - \frac{1}{D_{12}} \right) \tilde{\xi}_2 + \frac{1}{D_{12}}
\]

\[
= \frac{1 - \tilde{\xi}_2}{D_{13}} + 2 \frac{\tilde{\xi}_2}{D_{12}} - \frac{\tilde{\xi}_2}{D_{23}} + \frac{1}{D_{12}}
\]

where the inequality comes from applying Lemma 1.

This last line is a linear equation in \( \tilde{\xi}_2 \), so for \( \tilde{\xi}_2 \in [0, 1] \) the minimum value will be achieved at one of the interval end points. Therefore we get:

\[
2\tilde{\alpha}_1 - (\tilde{\alpha}_2 + \tilde{\beta}_1) \geq \min \left\{ \frac{1}{D_{13}} + \frac{1}{D_{12}}, \frac{3}{D_{12}} - \frac{1}{D_{23}} \right\} > 0,
\]

where the positivity comes from the assumption that \( 3D_{23} > D_{12} \).

For the second line of the matrix, \( A_{\text{sym}} \), one gets:

\[
2\tilde{\beta}_2 - (\tilde{\alpha}_2 + \tilde{\beta}_1) \geq \min \left\{ \frac{1}{D_{23}} + \frac{1}{D_{12}}, \frac{3}{D_{12}} - \frac{1}{D_{13}} \right\} > 0,
\]
here the positivity comes from the assumption that $3D_{13} > D_{12}$.

By the Gershgorin theorem the matrix has positive eigenvalues, so we can conclude that it is positive definite.

\begin{proof}

To prove the inf-sup condition for $b(\cdot, \cdot)$ we will make use of the following lemma from [16]:

**Lemma 2.** For any $v \in L^2(\Omega)$ there exists a $p \in H(div; \Omega)$ such that $\nabla \cdot p = -v$ and that satisfies the following inequality:

$$||p||_{H(div; \Omega)} \leq \left( \sqrt{1 + C^2_\Omega} \right) ||v||_{L^2(\Omega)},$$

where $C_\Omega$ is the constant in the Poincare inequality for the domain $\Omega$.

We can now prove the following proposition:

**Proposition 2.** The bilinear form $b(\cdot, \cdot)$ for the Maxwell-Stefan problem, satisfies the following inf-sup condition:

$$\inf_{v \in V} \sup_{p \in Q} \frac{b(p, v)}{||v||_V ||p||_Q} \geq \mu,$$

for some $\mu > 0$.

**Proof.** Let $p_1$ and $p_2$ be functions in $H(div; \Omega)$ such that $\nabla \cdot p_i = -v_i$, $i = 1, 2$, as in Lemma 2. Then we have:

\[
\begin{align*}
\frac{b(p, v)}{||v||_V} &= \frac{\int_\Omega (-v_1 \nabla \cdot p_1 - v_2 \nabla \cdot p_2) \, dx}{||v_1||_V^2 + ||v_2||_V^2} \\
&= \frac{\left( ||p_1||_{L^2(\Omega)}^2 + ||p_2||_{L^2(\Omega)}^2 \right)}{\sqrt{||v_1||_{L^2(\Omega)}^2 + ||v_2||_{L^2(\Omega)}^2}} \\
&\geq \frac{1}{\sqrt{1 + C^2_\Omega}} ||p||_Q,
\end{align*}
\]
where the inequality comes from Lemma 2. This leads to the following using the above $p_i$:

\[
\sup_{\tilde{p} \in Q} \frac{b(\tilde{p}, v)}{\|\tilde{p}\|_Q} \geq \frac{\int_\Omega (-v_1 \nabla \cdot p_1 - v_2 \nabla \cdot p_2) \, dx}{\|p\|_Q} \geq \frac{1}{\sqrt{1 + C_{\Omega}^2}} \|v\|_V.
\]

The above is equivalent to the proposition since $\frac{1}{\sqrt{1 + C_{\Omega}^2}} > 0$.

We now prove the following theorem:

**Theorem 2.** There exists a unique solution $(J, \xi) \in Q_g \times V$ to the mixed formulation of the linearized Maxwell-Stefan equations, when the binary diffusion coefficients satisfy $3D_{23} > D_{12}$ and $3D_{13} > D_{12}$ and when $c_{tot} \in C(\Omega)$.

**Proof.** The existence of a solution $(J, \xi) \in Q_g \times V$ is a direct application of Theorem 1, Proposition 1, and Proposition 2. The coercivity over all $Q$ implies the coercivity over $\text{Ker}(B)$.

Uniqueness is addressed in the following way. If $J = J_0 + J_g$ (See Remark 1 above), then $J_0$ will be defined uniquely for a given $J_g$. Now consider two solutions to the Maxwell-Stefan problem, $(J^1, \xi^1)$ and $(J^2, \xi^2)$. Let $\tilde{J} = J^1 - J^2$ and $\tilde{\xi} = \xi^1 - \xi^2$. We have that $\tilde{J} \in Q_0$ since $J^1 \cdot \nu = J^2 \cdot \nu$ on $\Gamma_N$ and $\tilde{\xi} = 0$ on $\Gamma_D$. So $(\tilde{J}, \tilde{\xi}) \in Q_0 \times V$ is a solution to:

\[
a(\tilde{J}, q) + b(q, \tilde{\xi}) = 0, \forall q \in Q_0,
b(\tilde{J}, v) = 0, \forall v \in V.
\]

By taking $q = \tilde{J}$ and $v = \tilde{\xi}$ we can combine the above equations to get:

\[
a(\tilde{J}, \tilde{J}) = 0.
\]

The coerciveness of $a(\cdot, \cdot)$ implies that $\tilde{J} = 0$. The system is therefore equivalent to:

\[
b(q, \tilde{\xi}) = 0, \forall q \in Q_0.
\]

For any $q_i \in (D(\Omega))^d \subset H(div; \Omega)$, we have

\[
0 = \int_\Omega \tilde{\xi}_i \nabla \cdot q_i \, dx = - \langle \nabla \tilde{\xi}_i, q_i \rangle_{D'(\Omega) \times D(\Omega)}.
\]
Therefore we have that \( \nabla \tilde{\xi}_i = 0 \) in \( D'(\Omega) \). Since \( \xi_i \) belongs to \( L^2(\Omega) \) we have that \( \xi_i \) coincides almost everywhere with a constant function \([17, \text{Corollary 2.1, p.9}]\). Since \( \xi \) is a constant function we have that \( \xi_i \in H^1(\Omega) \).

Now for \( q_i \in Q_0 \) we get:

\[
0 = \int_{\Omega} \tilde{\xi}_i \nabla \cdot q_i \, dx \\
= - \int_{\Omega} \nabla \tilde{\xi}_i \cdot q_i \, dx + < q_i \cdot \nu, \tilde{\xi}_i >_{\Gamma} \\
= < q_i \cdot \nu, \tilde{\xi}_i >_{\Gamma},
\]

for all \( q \cdot \nu \in H^{-1/2}(\Gamma_D) \). This implies that \( \tilde{\xi}_i = 0 \) in \( H^{1/2}(\Gamma_D) \), and since \( \tilde{\xi}_i \) is constant, we obtain that \( \tilde{\xi}_i \) is zero everywhere on \( \Omega \).

Since \( \tilde{J} \) and \( \tilde{\xi} \) are zero we obtain the uniqueness of solutions to the linearized Maxwell-Stefan problem.

\[\square\]

6. Finite element methods and error estimates

Let \( T_h \) be a regular triangularization of \( \Omega \), with \( h \) the maximum diameter of the elements. The flux space will be approximated with the \( k \)-th order Raviart-Thomas elements \( RT^k \), \([18]\) or \( k+1 \)-th order Brezzi-Douglas-Marini elements \( BDM^{k+1} \)\([19]\). For the analysis of the mixed finite element method we will restrict our attention to the Raviart-Thomas elements. The analysis is very similar when using the Brezzi-Douglas-Marini elements \([15, \text{Sec III.3}]\).

The concentration space will be approximated with \( k \)-th order Lagrange elements. The notation \( P^k \) refers to the space of piecewise polynomial functions which are continuous across element boundaries and \( P^k_{dc} \) refers to the space where functions are not necessarily continuous across element boundaries. So we have the following spaces:

\[
V_h = \{ v_h \in V | v_{h,i} \in P^k_{dc} \}, \\
Q_{h,g} = \{ q_h \in Q | q_{h,i} \in RT^k, \gamma_{\nu,\Gamma_N}(q_{h,i}) = g_i \text{ on } \Gamma_N \},
\]

The numerical method proceeds with a fixed point as follows: For an initial guess \( \tilde{\xi}_h \), find \( (J_h, \xi_h) \in Q_{h,g} \times V_h \) such that,
\[
\int_{\Omega} \left\{ \frac{J_{h,i} \cdot q_{h,i}}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_{h,i} \cdot J_{j,h} \cdot q_{h,i} - \xi_{j,h} J_{h,i} \cdot q_{h,i}) \right\} \, dx 
\]

\[
- \int_{\Omega} \xi_{h,i} \nabla \cdot q_{h,i} \, dx = -< q_{h,i} \cdot \nu, f_{i} >_{\Gamma_{D}}, \quad (24)
\]

\[
\int_{\Omega} v_{h,i} \nabla \cdot J_{h,i} \, dx = \int_{\Omega} r_{i} v_{h,i} \, dx, \quad (25)
\]

for all \( v_{h} \in V_{h} \) and \( q_{h} \in Q_{h,0} \).

Now let the new guess be \( \bar{\xi}_{h,i} := \sigma \xi_{h,i} + (1 - \sigma) \xi_{h,i} \) for \( \sigma \in [0, 1] \). Solve Equations (24) and (25) until \( ||\xi_{h} - \bar{\xi}_{h}||_{V} \) is less than some tolerance.

With our mixed finite methods, the nonlinearity is only quadratic, simplifying the implementation of Newton-Raphson method compared to Standard \( P_{k} \) methods. This is of course done at the expense of solving a larger linear system, given the extra unknowns \( J_{h,i} \), but at the end the fluxes are available with equal accuracy if a stable pair of finite element spaces is chosen. For instance, for the \( RT^{0}-P_{0} \) method this adds one DOF per edge (shared between neighboring elements) for each flux \( J_{h,i} \) on top of the single DOF per element for the mole fraction \( \xi_{h,i} \).

To analyze the stability and convergence of mixed finite element methods we will make use of the following theorem [15, section 2.2]:

**Theorem 3.** Let \( V \) and \( Q \) be Hilbert spaces and let \( a(\cdot, \cdot) : Q \times Q \rightarrow \mathbb{R} \) and \( b(\cdot, \cdot) : Q \times V \rightarrow \mathbb{R} \) be bounded linear forms with associated operators \( A : Q \mapsto Q^{*} \) and \( B : Q \mapsto V^{*} \).

Moreover let \( V_{h} \subset V \) and \( Q_{h} \subset Q \) be finite dimensional subspaces and \( A_{h} : Q_{h} \rightarrow Q_{h}^{*} \) and \( B_{h} : Q_{h} \rightarrow V_{h}^{*} \) the operators associated to the restriction of \( a(\cdot, \cdot) \) and \( b(\cdot, \cdot) \) to their respective finite dimensional subspaces.

Now assume the following are satisfied for two constants \( \lambda_{h} \) and \( \mu_{h} \):

(i) The bilinear form \( \left. a(\cdot, \cdot) \right|_{V_{h}\times V_{h}} \) satisfies the following coercivity condition on \( \text{Ker}(B_{h}) \):

\[
a(p_{h}, p_{h}) \geq \lambda_{h} \|p_{h}\|_{Q}^{2} > 0 \quad \forall p_{h} \in \text{Ker}(B_{h}). \quad (26)
\]

(ii) The bilinear form \( \left. b(\cdot, \cdot) \right|_{V_{h}\times Q_{h}} \) satisfies the following inf-sup condition:

\[
\inf_{v_{h} \in V_{h} \setminus \text{Ker}(B_{h})} \sup_{q_{h} \in Q_{h}} \frac{b(q_{h}, v_{h})}{\|q_{h}\|_{Q} \|v_{h}\|_{V}} \geq \mu_{h} > 0. \quad (27)
\]
Then for any $f \in Q^*$ and $r \in \text{Im}(B)$ the finite dimensional saddle point problem has a solution $(J_h, \xi_h) \in Q_h \times V_h$, where $J_h$ is uniquely determined and $\xi_h$ is unique up to an element of $\text{Ker}(B_h^*)$.

If the mixed finite element method converges and the constants $\lambda_h = \lambda$ and $\mu_h = \mu$ are independent of $h$, then we have the following a priori error estimates:

\[
||J - J_h||_Q \leq (1 + \frac{||a||}{\lambda})(1 + \frac{||b||}{\mu}) \inf_{q_h \in Q_h} ||J - q_h||_Q + \frac{||b||}{\lambda} \inf_{v_h \in V_h} ||\xi - v_h||_V, \quad (28)
\]

\[
||\xi - \xi_h||_V \leq (1 + \frac{||b||}{\mu}) \inf_{v_h \in V_h} ||\xi - v_h||_V + \frac{||a||}{\mu} \inf_{q_h \in Q_h} ||J - q_h||_Q. \quad (29)
\]

**Remark 2.** If $\text{Ker}(B_h) \subset \text{Ker}(B)$, then we have the following error estimate:

\[
||J - J_h||_Q \leq (1 + \frac{||a||}{\lambda})(1 + \frac{||b||}{\mu}) \inf_{q_h \in Q_h} ||J - q_h||_Q. \quad (30)
\]

To apply Theorem 3, suitable finite element space combinations must be chosen such that the coercivity and the inf-sup conditions are satisfied. For this, we choose the $RT^k/P^k_{dc}$ combinations for discretizing $J$ and $\xi$, respectively. This choice of spaces has the property that $\text{div}(RT^k) = P^k_{dc}$. This means that the operator $B_h$ is just the restriction of $B$ to the subspace $RT^k$. So the coercivity condition on $a(\cdot, \cdot)$ over $\text{Ker}(B_h)$ is implied by the coercivity condition over $\text{Ker}(B)$. We will apply the following lemma to analyze the inf-sup condition (27):

**Lemma 3.** Assume there exists a $\mu > 0$ such that $\forall v \in L^2(\Omega), \exists q \in Q, q \neq 0$, that satisfies the continuous inf-sup condition (15). There exists an operator $\tau_h : Q \rightarrow RT^k$ such that:

\[
(1) \int_{\Omega} v_{h,i} \nabla \cdot (q_i - \tau_h(q_i)) = 0 \quad i = 1, 2, 
\]

\[
(2) \|\tau_h(q)\|_Q \leq C_* ||q||_Q, 
\]

**Proof.** See [16, Sec 7.2.2.].

We can now prove the following proposition:

**Proposition 3.** The inf-sup condition for the discrete problem (27) is satisfied for $Q_h = RT^k$ and $V_h = P^k_{dc}$.

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Proof. By Theorem 2 there exists a \( \mu \) such that \( \forall v \in V, \exists q \in Q, q \neq 0 \) that satisfies the continuous inf-sup condition, equation (13). Since \( q_i \in H(\text{div}; \Omega) \), by Lemma 3 there exists an operator \( \tau_h : H(\text{div}; \Omega) \rightarrow RT^k \) that satisfies Equations (31) and (32). Now we can apply the Fortin lemma [15, Prop. 2.8, p. 58] and conclude that the inf-sup condition for the discrete problem is satisfied for a constant independent of \( h \). \( \square \)

There exists an interpolation operator onto the space \( P^k_{dc} \) with the following property [16, p.90]:

**Proposition 4.** The interpolation operator \( \Pi_h : V \rightarrow P^k_{dc} \) satisfies the following error estimate for \( k \geq 0 \):

\[
\|v - \Pi_h v\|_V^2 \leq c h^{k+1} |v|_{k+1, \Omega} \quad \forall v \in (H^{k+1}(\Omega))^2,
\]

where \( |v|_{k+1, \Omega} \) is the \( H^{k+1}(\Omega) \) semi-norm.

We will also use the following interpolation error estimate from [16, Sec. 7.2.2]

**Proposition 5.** Let \( v \in P^k_{dc} \). There exists an interpolator \( \tau_h : (H(\text{div}; \Omega))^2 \rightarrow RT^k \) satisfying the following error estimate for \( q \in (H^{k+1}(\Omega))^2 \):

\[
\|\tau_h(q) - q\|_Q \leq C h^{k+1} \left( |q|_{k+1, \Omega} + \sum_{i=1}^{2} |\text{div}(q_i)|_{k+1, \Omega} \right)
\]

**Theorem 4.** For ternary diffusion if the binary diffusion coefficients satisfy \( 3D_{23} > D_{12} \) and \( 3D_{13} > D_{12} \). The mixed finite element method for the linearized Maxwell-Stefan problem defined by Equations (24) and (25) has a solution \( (J_h, \xi_h) \in (RT^k)^2 \times (P^k_{dc})^2 \), where \( J_h \) and \( \xi_h \) are unique. Additionally if the solution \( (\xi, J) \in (H^{k+1}(\Omega))^2 \times (H^{k+1}(\Omega))^2 \), then the following error estimates are satisfied:

\[
||\xi - \xi_h||_V \leq C h^{k+1} (|\xi|_{k+1, \Omega} + |J|_{k+1, \Omega} + |\text{div}(J)|_{k+1, \Omega}),
\]

\[
||J - J_h||_V \leq C h^{k+1} (|J|_{k+1, \Omega} + |\text{div}(J)|_{k+1, \Omega}),
\]

where \( |\cdot|_{k+1, \Omega} \) denotes the \( H^{k+1} \) semi-norm over \( \Omega \).

Proof. By proposition 3 the discrete inf-sup condition is satisfied, and the coercivity of the bilinear form \( a(\cdot, \cdot) \) over \( RT^k \) is established by the coercivity
over \((H(div; \Omega))^2\). Therefore, by Theorem 2, we have the existence of a solution \((J_h, \xi_h) \in (RT^k)^2 \times (P_{dc}^k)^2\).

Since \(\text{Ker}(B_h) \subset \text{Ker}(B)\) we have the following error estimates from [15]:
\[
\|\xi - \xi_h\|_V \leq c_1 \inf_{v_h \in P_{dc}^k} \|\xi - v_h\|_V + c_2 \inf_{q_h \in RT_k} \|J - q_h\|_Q,
\]
\[
\|J - J_h\|_V \leq c_3 \inf_{q_h \in RT_k} \|J - q_h\|_Q,
\]
where \(c_1 = (1 + \|b\|_\mu), \ c_2 = \|a\|_\mu,\ \text{and}\ \ c_3 = (1 + \|a\|_\lambda)(1 + \|b\|_\mu)\).

We use the interpolation error estimate, to get an error estimate for \(\xi\) in terms of semi-norms:
\[
\inf_{v_h \in P_{dc}^k} \|\xi - v_h\|_V \leq \|\xi - \Pi_h \xi\|_V \leq c h^{k+1} |\xi|_{k+1, \Omega} \quad \forall \xi \in (H^{k+1}(\Omega))^2,
\]
with a constant \(c\) independent from \(h\) and \(\xi\).

We proceed in the same way using the above interpolator to get an error estimate for \(J\) in terms of the \(H^{k+1}\) semi-norm:
\[
\inf_{q_h \in RT_k} \|J - q_h\|_Q \leq \|J - \tau_h J\|_Q \leq C h^{k+1} (|J|_{k+1, \Omega} + |div(J)|_{k+1, \Omega}),
\]
where this holds for all \(J \in (H^{k+1}(\Omega))^2\). We can now substitute the estimates for the infimums of the norms into the error estimates above to get equations (35) and (36).

\[
\square
\]

7. Numerical results

The finite element methods were implemented using the open source software FreeFem++[20]. The software was used to construct the meshes, to build the finite element functions, and for plotting the solutions.

The function \(\bar{\xi}_i\) were initially taken to be zero everywhere in the domain, then the linearized Stefan Maxwell problem was solved numerically using the direct solver, UMFPACK. The solution \(\xi_h\) was compared to the previous guess \(\xi_h\) by computing \(||\xi_h - \bar{\xi}_h||_V\). If this norm was greater than \(10^{-10}\), the functions \(\xi_{h,i}\) were updated as described above, otherwise the fixed point iterations were stopped. We used only this simple fixed point method as it proved to be very efficient except for one test case where more iterations were required.
7.1. Analytic test case

A test case was constructed on a domain $\Omega$ with boundary conditions and reaction rates such that the solution to the Maxwell-Stefan problem was known exactly. The $L^2$-error between the exact solution and the numerical approximation was then computed for varying mesh sizes. This was then used to determine the order of convergence of the mixed finite element methods.

We consider the domain $\Omega = [0,1] \times [0,1]$ and proceed with the method of manufactured solution where an analytical solution is provided and the data (right-hand side and boundary condition) are adjusted so the Maxwell-Stefan problem is satisfied. Define two functions $f_1$ and $f_2$ as follows:

$$f_1 = \begin{cases} \frac{\sinh(\frac{x}{2})\sin(\frac{\pi y}{2})}{\sinh(\frac{\pi y}{2})} & x \in [0,1], y = 1 \\ \frac{\sinh(\frac{\pi x}{2})}{\pi^2} & x = 1, y \in [0,1] \\ 0 & \text{Otherwise} \end{cases}$$

$$f_2 = \begin{cases} \frac{\cosh(\frac{x}{2})\cos(\frac{\pi y}{2})}{\cos(\frac{\pi y}{2})} & x \in [0,1], y = 1 \\ \frac{\cosh(\frac{\pi x}{2})}{\pi^2} & x \in [0,1], y = 0 \\ 0 & \text{Otherwise} \end{cases}$$

For this test case Dirichlet boundary conditions are used on all $\Gamma$, i.e. $\Gamma_D = \Gamma$. The reaction rates are defined by two functions $r_1$ and $r_2$ in the domain $\Omega$ as follows:

$$r_1 = \left( \frac{\alpha_{21}}{\chi} - \frac{\alpha_{21} \tilde{\beta}_2}{D_{12} \chi^2} + \frac{\tilde{\alpha}_2 \alpha_{12}}{D_{23} \chi^2} \right) \left( \frac{\sin(\pi x/2) + \sinh(\pi y/2)}{4\pi^2} \right)$$

$$r_2 = \left( \frac{\alpha_{12}}{\chi} - \frac{\alpha_{12} \tilde{\alpha}_1}{D_{23} \chi^2} + \frac{\tilde{\beta}_1 \alpha_{21}}{D_{13} \chi^2} \right) \left( \frac{\sin(\pi x/2) + \sinh(\pi y/2)}{4\pi^2} \right),$$

where the $\chi$ in the above equations is defined as follows:

$$\chi = \frac{1}{D_{13} D_{23}} - \frac{\alpha_{12} \xi_1}{D_{23}} - \frac{\alpha_{21} \xi_2}{D_{13}}.$$
\[ \xi_1 = \frac{\sin(\pi x/2) \sinh(\pi y/2)}{\pi^2}, \quad (40) \]
\[ \xi_2 = \frac{\cos(\pi x/2) \cosh(\pi y/2)}{\pi^2}, \quad (41) \]
\[ J_1 = \frac{-\tilde{\beta}_2}{\chi} \nabla \xi_1 + \frac{\tilde{\alpha}_2}{\chi} \nabla \xi_2, \quad (42) \]
\[ J_2 = \frac{\tilde{\beta}_1}{\chi} \nabla \xi_1 - \frac{\tilde{\alpha}_1}{\chi} \nabla \xi_2. \quad (43) \]

The problem was solved using the finite element methods described in the previous section with a uniform triangular mesh. The binary diffusion coefficients were taken to be as follows: \( D_{12} = 15 \), \( D_{13} = 10 \), and \( D_{23} = 5 \). The concentration was assumed to be uniform everywhere, \( c_{\text{tot}} = 1 \). The \( L^2 \)-errors on the mole fractions (\( E_{\xi} \)) and the fluxes (\( E_J \)) were computed with varying mesh sizes using different mixed and standard finite element methods. Using \( \sigma = 1 \) the fixed point method usually converges in about 6 iterations for this test case.

The mixed finite element spaces considered are \( RT^0/P^0_{dc} \), \( RT^1/P^1 \), \( RT^1/P^1_{dc} \) and \( BDM^1/P^0_{dc} \), where the first element refers to the space \( Q_h \) for fluxes and the second refers to the space \( V_h \) for mole fractions. Note that the space \( RT^1/P^1 \) does not fall under the hypothesis of Theorem 3, hence it is not clear what should be the expected convergence rate in this case. The problem was also solved using standard finite element methods with finite element spaces \( P^1 \) and \( P^2 \).

A comparison of the exact functions with some of the mixed finite element approximations can be seen in Figures 1 and 2. In all cases, the finite element solutions for the concentrations look very similar to the exact solutions. The \( RT^0/P^0_{dc} \) solution shows small wiggles in the mole fraction isolines due to the piecewise constant approximation of this variable. On Fig. 2, the flux computed by the \( RT^1/P^1_{dc} \) mixed finite element method looks similar to the exact flux. We only show the flux \( J_1 \) for one method but the trend is the same for \( J_2 \) and the other finite element methods.

The \( L^2 \) errors and order of convergence for all these methods are summarized in Figure 3 and Table 1. For \( RT^0/P^0_{dc} \) and \( BDM^1/P^0_{dc} \) it can be seen that both the mole fractions and the fluxes have a first order convergence rate. Similarly \( RT^1/P^1_{dc} \) has a second order convergence rate in both variables. The standard \( P^k \) methods have the same \( k + 1 \) order convergence in
the concentration variable that the $RT^k/P^k_{dc}$ method has. However, when we attempt to recover the flux from the standard finite element solution we lose an order of accuracy.

Table 1: The slopes of the least squares best fit to the $-\ln(E)$ vs. $-\ln(h)$ data for each of the finite element methods

<table>
<thead>
<tr>
<th>Finite Element Method</th>
<th>Slope for $\xi$</th>
<th>Slope for $J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard $P^2$</td>
<td>3.0001</td>
<td>2.0059</td>
</tr>
<tr>
<td>Standard $P^1$</td>
<td>1.9999</td>
<td>0.9999</td>
</tr>
<tr>
<td>$RT^1/P^1_{dc}$</td>
<td>1.9997</td>
<td>1.9997</td>
</tr>
<tr>
<td>$RT^0/P^0_{dc}$</td>
<td>0.9988</td>
<td>0.9988</td>
</tr>
<tr>
<td>$RT^1/P^1$</td>
<td>2.0073</td>
<td>1.0038</td>
</tr>
<tr>
<td>$BDM^1/P^0_{dc}$</td>
<td>1.0000</td>
<td>1.0038</td>
</tr>
</tbody>
</table>

For the molar flux we find that the $RT^k/P^k_{dc}$ methods have a higher order and better absolute error than the standard $P^k$ methods and the same order and similar absolute error as the standard $P^{k+1}$ methods. The flux in the $BDM^1/P^0_{dc}$ method was much more accurate than the flux calculated using $RT^0/P^0_{dc}$ but less accurate than higher order $RT^1/P^1_{dc}$ method. Extrapolating from this would suggest that numerical solutions found using the $BDM^2/P^1$ method would be as accurate as the $RT^1/P^1_{dc}$ and $P^1$ methods in concentration but much more accurate than any of the tested methods in the flux variables.

7.2. Mazumder test case

In this test case we consider a box of 10cm by 10cm with three openings, one opening on the bottom, one on the top and one to the left, as seen in Figure 4. No flux boundary conditions are used away from the openings ($\Gamma_N$), and Dirichlet boundary conditions at the openings ($\Gamma_D$), assuming only one gas is flowing into the box at each opening. There are two variants of this test case. The first is the one originally proposed in [9] where all the binary diffusion coefficients are equal and the second proposed in [7] where all three binary diffusion coefficients are different. For this test case we take our gases to be $N_2$, $H_2O$ and $H_2$.

For these test cases, mixed finite element methods were applied to the mass formulation of the Maxwell-Stefan equations as in [7]. This way the mass fractions, $Y_i$, and mass fluxes, $j_i$, could be computed directly. A simple
Figure 1: Comparison of the exact and numerical solutions for $\xi_1$. Results are shown for the mesh with 3200 elements.
conversion of the variables could have worked but we give their formulation in terms of masses for completeness.

The mass formulation is found using the following identities:

\[ \xi_i = \frac{MY_i}{m_i} \quad \text{and} \quad J_i = \frac{j_i}{m_i}, \quad (44) \]

where \( m_i \) is the mass of species \( i \) and \( M \) is the mass of the mixture. The concentration \( c_{tot} \) was also replaced with \( \rho/M \), where \( \rho \) is the density of the mixture. The mass formulation of the Maxwell-Stefan equations is:
Figure 3: Plots comparing the errors of the different finite element methods with respect to the number of elements in the mesh. A comparison of the errors on mole fractions is shown in (a) and a comparison of the error on molar fluxes is shown in (b)
Figure 4: Diagram showing the geometry for test cases 2 and 3. The arrows show which gas is flowing through the opening.

\[-\nabla \frac{MY_i}{m_i} = \frac{M^2}{\rho} \sum_{j=1}^{n} \frac{Y_{ji}j_i - Y_{ij}j_i}{m_im_jD_{ij}},\]  
\[\nabla \cdot \frac{j_i}{m_i} = r_i,\]  
\[\sum_{i=1}^{n} Y_i = 1,\]  
\[\sum_{i=1}^{n} j_i = 0.\]  

The mass formulation of Maxwell-Stefan equations rewrites into a mixed variational formulation as for the equations written in molar form. When this is done we arrive at the following bilinear form \( a(\cdot, \cdot) \) for ternary diffusion:

\[ a(j, q) = \int_{\Omega} \frac{M^2}{\rho} \left( \left( \frac{1}{m_1m_3D_{13}} - \nabla_2\alpha \right) j_1 + \nabla_1\alpha j_2 \right) \cdot q_1 \, dx \]  
\[+ \int_{\Omega} \frac{M^2}{\rho} \left( \nabla_2\beta j_1 + \left( \frac{1}{m_2m_3D_{23}} - \nabla_1\beta \right) j_2 \right) \cdot q_2 \, dx,\]
where \( \alpha = \frac{1}{m_1 m_3 D_{13}} - \frac{1}{m_1 m_2 D_{12}} \) and \( \beta = \frac{1}{m_2 m_3 D_{23}} - \frac{1}{m_1 m_2 D_{12}} \). For the total mass and density we have the following:

\[
\rho = Y_1 m_1 + Y_2 m_2 + Y_3 m_3, \quad (51)
\]

\[
M = \frac{1}{\frac{Y_1}{m_1} + \frac{Y_2}{m_2} + \frac{Y_3}{m_3}}. \quad (52)
\]

The other parts of the mixed formulation are found just by substituting (44). With this formulation we can now proceed with the next two test cases.

For the Mazumder test case all the binary diffusion coefficients are taken to be equal to 10 cm\(^2\)/s. The value of the coefficient will not change the solution for the mass fractions [7], it will however change the flux. A non-uniform mesh was created using FreeFEM++’s “buildmesh” function.

The computation was performed using the mesh shown on Figure 5 and the mixed finite element method \( RT^1/P^1_{dc} \). The simulation took 631 nonlinear iterations for \( \sigma = 0.03 \). The heavy under relaxation was necessary to achieve convergence of the fixed point. The calculation required a CPU time of 22 minutes. Newton-Raphson method would easily improve the convergence of the fixed point iterations. Computations were also performed using the RT0/P0 method and were visually similar to the RT1/P1dc method. The main difference was that the isolines for the variable \( Y_i \) were jagged in the RT0/P0 solution. This is due to the numerical solutions being constant on each element. The plots for the RT1/P1dc method can be seen in Figures 6 and 7. The mass fractions in [7] were calculated on an 80x80 grid using Lagrange elements (\( P^2 \)). Graphically there is no difference between the two results. Fluxes are not given in [7] to be compared to our solutions.

The third test case was presented in [7]. It uses the same domain and boundary conditions as the previous test case, the difference comes from the fact that the binary diffusion coefficients are no longer taken to be equal. The coefficients were taken to be \( D_{N_2-H_2O} = 1, D_{N_2-H_2} = 10, \) and \( D_{H_2-H_2O} = 100 \). The fixed point converged in 631 iterations (\( \sigma = 0.03 \)) and required a CPU time of 22 minutes. Since the constants \( \alpha \) and \( \beta \) are not zero in either test case 2 or 3 the fixed point iteration converges in the same number of iterations. The mass fractions shown in [7] were computed using \( P^2 \) elements on a mesh with 80x80 grid (6400 grid points). Graphically the mass fraction plots in [7] look the same as our solution computed using the \( RT^1/P^1_{dc} \) method on a grid with 1135 points (See Figure 8). Plots for the mass fluxes are
shown in Figure 9. Here we can see that there is a lower nitrogen mass flow between the nitrogen inlet and the water inlet and a larger mass flow between the nitrogen inlet and the hydrogen inlet than for the case of equal binary diffusion coefficients. Similar remarks can be made for the other two species. As in the previous test case, there is no flux data to compare our solution to.

8. Conclusion

A main advantage of mixed finite element methods is that it allows one to solve the Maxwell-Stefan equations for the species fluxes and concentrations to the same order. These methods do not require the inversion of the Maxwell-Stefan equations. This compares favorably to standard finite element methods used so far, which require the inversion of the Maxwell-Stefan equations and give at best a convergence one order lower on the fluxes than on the concentrations. This comes from the fact that the fluxes must be recovered from the gradients of the numerical concentrations. These effects were replicated explicitly in our first numerical test case. It was also seen that mixed finite element methods gave similar absolute errors for the concentrations as standard finite element methods but achieved optimal convergence order on the fluxes as well.
Figure 6: Plots of the mass fractions for the Mazumder steady state test where all binary diffusion coefficients are taken to be $10 \, \text{cm}^2/\text{s}$

The well-posedness of the mixed variational formulation and the convergence of the mixed finite element methods were proved using constraints on the bilinear diffusion coefficients. The mixed finite element method also converged for our third test case even though the binary diffusion coefficients were well outside of the range used in Theorem 2, suggesting that less restrictive versions of Theorem 2 and 4 could be proven. It should be noted that there are more general versions of Theorems 1 and 3, where the coercivity condition on $a(\cdot, \cdot)$ is replaced by a pair of inf-sup conditions. It is possible that the theoretical results for the mixed finite element methods applied
Figure 7: Plots of the mass fluxes for the Mazumder steady state test where all binary diffusion coefficients are taken to be $10 \text{ cm}^2/\text{s}$

to Maxwell-Stefan equations could be improved upon by applying the more general theory for abstract saddle point problems.

From a practical standpoint, our mixed finite element approach for the Maxwell-Stefan equations could easily be improved by using a better fixed point method. For the highly nonlinear third test case the mixed finite element method converged in 631 iterations. We used a heavily under-relaxed fixed point method. The number of iterations could certainly be reduced by applying a Newton-Raphson method. The solution of the larger linear system associated with the mixed methods could also be improved.
Figure 8: Plots of the mass fractions for the steady state test where the binary diffusion coefficients are taken as $D_{N_2-H_2O} = 1\text{cm}^2/\text{s}$, $D_{N_2-H_2} = 10\text{cm}^2/\text{s}$, and $D_{H_2-H_2O} = 100\text{cm}^2/\text{s}$
Figure 9: Plots of the mass fluxes for the steady state test where the binary diffusion coefficients are taken as $D_{N_2-H_2O} = 1 \text{cm}^2/\text{s}$, $D_{N_2-H_2} = 10 \text{cm}^2/\text{s}$, and $D_{H_2-H_2O} = 100 \text{cm}^2/\text{s}$.
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References


