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

Michael McLeod

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Mathematics ¹

Department of Mathematics and Statistics
Faculty of Science
University of Ottawa

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Abstract

The Stefan-Maxwell 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 make finding solutions difficult, so numerical methods are often used. In the engineering literature the system is inverted to write fluxes as functions of the species gradient before any numerical method is applied. In this thesis it is shown that employing a mixed finite element method makes the inversion unnecessary, allowing the numerical solution of Stefan-Maxwell equations in their primitive form. The plan of the thesis is as follows, first a mixed variational formulation will be derived for the Stefan-Maxwell equations. The nonlinearity will be dealt with through a linearization. Conditions for well-posedness of the linearized formulation are then determined. Next, the linearized variational formulation is approximated using mixed finite element methods. The finite element methods will then be shown to converge to an approximate solution. A priori error estimates are obtained between the solution to the approximate problem and the exact solution. The convergence order is then verified through an analytic test case and compared to standard methods. Finally, the solution is computed for another test case involving the diffusion of three species and compared to other methods.

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Chapter 1

Introduction

1.1 Stefan-Maxwell Equations

The Stefan-Maxwell equations describe the process of diffusion in a mixture of multiple chemical species. They were developed independently by Maxwell and Stefan and serve as a generalization of other diffusion laws. Simpler diffusion models such as Fick's Law [15] have been shown by Duncan and Toor to give inaccurate results in ternary mixtures [11]. Therefore the Stefan-Maxwell equations are preferred. The Stefan-Maxwell equations have applications to biology and chemical engineering. A simple derivation of the equations is presented here. A more detailed discussion of the physics behind the Stefan-Maxwell equations can be found in [15] or [22].

Physically the system represents a mixture of n ideal gases, where each species i has a mole fraction of ξ_i , in moles per unit volume, 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: For $i = 1, 2, \dots, n$:

$$\nabla \cdot J_i = r_i.$$

The motion of the gases will cause the particles of one 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 $i = 1, 2, \dots, n$:

$$-\nabla \xi_i = \frac{1}{c_{tot}} \sum_{j=1}^n \frac{\xi_j J_i - \xi_i J_j}{D_{ij}},$$

where D_{ij} is the binary diffusion coefficient between species i and species j , and $c_{tot} > 0$ is the total concentration of the mixture. The coefficients D_{ij} and D_{ji} are taken to be equal [15].

Consider a domain $\Omega \subset \mathbb{R}^d$, such that the boundary of Ω , Γ , is divided into two components, Γ_D and Γ_N . These components satisfy: $\Gamma_D \cap \Gamma_N = \emptyset$. On the boundary Γ_D , the molar fraction ξ_i is taken to be f_i . On Γ_N , with outward unit normal vector ν , the normal flux of species i , $J_i \cdot \nu$, is taken to be g_i . Since the variable ξ_i represents mole fractions, at any point in the domain the following condition holds:

$$\sum_{i=1}^n \xi_i = 1.$$

To define the full system we will make use of the following fact in [3, 16]:

$$\sum_{i=1}^n J_i = 0.$$

We will use the following definitions:

$$\xi = (\xi_1, \xi_2, \dots, \xi_n),$$

$$J = (J_1, J_2, \dots, J_n).$$

The Stefan Maxwell problem for steady n -ary diffusion becomes: Find (J, ξ) such that the following equations are satisfied in Ω for $i = 1, 2, \dots, n$:

$$-\nabla \xi_i = \frac{1}{c_{tot}} \sum_{j=1}^n \frac{\xi_j J_i - \xi_i J_j}{D_{ij}}, \quad (1.1.1)$$

$$\nabla \cdot J_i = r_i, \quad (1.1.2)$$

$$\sum_{i=1}^n \xi_i = 1, \quad (1.1.3)$$

$$\sum_{i=1}^n J_i = 0, \quad (1.1.4)$$

with the following boundary conditions on Γ :

$$\xi_i = f_i \quad \text{on} \quad \Gamma_D, \quad (1.1.5)$$

$$J_i \cdot \nu = g_i \quad \text{on} \quad \Gamma_N. \quad (1.1.6)$$

Remark: If all of the binary diffusion coefficients are taken to be equal to a value D , then the Stefan-Maxwell equations become:

$$J_i = -D\nabla\xi_i, \quad \text{for } i = 1, 2, \dots, n. \quad (1.1.7)$$

This equation is referred to as Fick's Law[15, 22].

The nonlinearity and the coupling terms in the Stefan-Maxwell equations make finding analytic solutions difficult or impossible, therefore numerical methods are necessary. In this thesis numerical solutions are found using mixed finite element methods. To set up the numerical method we need to establish a mixed variational formulation for the Stefan-Maxwell equations.

1.2 Mixed Variational Formulations

In this section mixed variational formulations are introduced by their application to the Poisson problem. The difference between a mixed variational formulation and a standard formulation, is that the mixed formulation solves for two variables simultaneously. A detailed look at mixed formulations can be found in [7, 20].

The Poisson problem is as follows: Find a function u in the domain $\Omega \subset \mathbb{R}^n$ such that:

$$\begin{aligned} -\Delta u &= r \quad \text{on } \Omega, \\ u &= f \quad \text{on } \Gamma. \end{aligned}$$

where Γ is the boundary of Ω .

To obtain the mixed formulation we make the following definition:

$$p = \nabla u.$$

We can now rewrite the Poisson equation as follows:

$$\begin{aligned} p - \nabla u &= 0 \quad \text{in } \Omega, \\ \nabla \cdot p &= -r \quad \text{in } \Omega. \end{aligned}$$

To find weak solutions of the above system, we multiply the first equation by a vectorial test function q , and the second equation by a scalar test function v . We then integrate both equations over the domain Ω . Finding weak solutions of the above differential equations is now a matter of solving the following problem: Find $(p, u) \in Q \times V$ satisfying:

$$\begin{aligned} \int_{\Omega} (p \cdot q + u \nabla \cdot q) \, dx &= \int_{\Gamma} f q \cdot \nu \, ds, \\ \int_{\Omega} v \nabla \cdot p \, dx &= - \int_{\Omega} r v \, dx, \end{aligned}$$

where ν is the outward unit normal vector to the boundary Γ .

To complete the mixed variational formulation we need to identify the spaces Q and V . In order for the above integrals to be defined, we require that the divergence of the functions p and q are in $L^2(\Omega)$. Therefore the space Q will be defined as:

$$H(\text{div}; \Omega) = \{q \in (L^2(\Omega))^n \mid \nabla \cdot q \in L^2(\Omega)\}, \quad (1.2.1)$$

and V will be taken to be $L^2(\Omega)$. Take $r \in L^2(\Omega)$ so that the integral in the right-hand side of the second equation is well-defined. The function f will be taken to be in $H^{1/2}(\Omega)$ so the boundary integral in the first equation is understood as the duality product of $q \cdot \nu \in H^{-1/2}(\Gamma)$ with $f \in H^{1/2}(\Gamma)$, see [23, p. 9]:

$$\int_{\Gamma} f q \cdot \nu ds := \langle q \cdot \nu, f \rangle_{H^{-1/2}(\Gamma) \times H^{1/2}(\Gamma)}.$$

This and related operators will be defined below.

The formulation above is now our mixed formulation for the Poisson equation. It allows us to solve simultaneously for both u and its gradient p .

The Stefan-Maxwell equations naturally lead to a mixed variational formulation where u stands for molar fractions and p represents the fluxes. Surprisingly enough, such a formulation and related mixed finite element methods have not yet been proposed for the Stefan-Maxwell equations, at least not that we know of.

1.3 Literature Review

The Stefan-Maxwell equations can be found in applications throughout the chemical engineering literature. The usual method for finding a numerical solution is to invert the system and apply the finite element method. In [1] a model for bone tissue growth using coupled Navier-Stokes and Stefan-Maxwell equations is described. The authors invert the Stefan-Maxwell equations to express the fluxes in terms of mass fractions before applying a finite element method using the finite element software Femlab. In [4] a benchmark for diffusion and fluid flow is introduced. The model used relies on an inversion of the Stefan-Maxwell equations before applying a finite element method to find the solution. A model of water transport in a fuel cell is

described in [14] using Stefan-Maxwell 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 scheme for Stefan-Maxwell equations is considered in [17]. The system is inverted so that the flux is written explicitly in terms of the mass fractions before any finite element scheme is applied. A finite volume approach is applied in [18] 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 numerically solve the Stefan-Maxwell equations. In [9] a finite difference scheme for the mole fractions and velocities is used to approximate the gradients of the mole fractions. The molar flux is expressed 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 [16] to study the phenomena of uphill diffusion. The Stefan-Maxwell equations are solved using a finite difference discretization, and the numerical method is shown to be second order and a condition for L^∞ -stability is found.

Recently work has been done looking at the mathematical properties of Stefan-Maxwell equations [3, 16]. In [16] conditions are imposed which show that if the initial functions ξ_i^{in} are nonnegative functions in $L^\infty(\Omega)$ then the Stefan-Maxwell equations admit unique smooth solutions for all time, moreover ξ_i remains nonnegative. It has been shown in [3] that the time dependent homogenous system is well-posed for a solution that is local in time. Additionally the same paper has shown that the mole fractions ξ_i are non-negative for the inhomogenous 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 Stefan-Maxwell equations in the context of mixed finite element methods. The system of equations naturally leads to

a mixed formulation. In this thesis, mixed finite element methods will be developed and applied to the Stefan-Maxwell equations and compared to previous work done.

1.4 Outline of the Thesis

The thesis is organized in the following way. In the second chapter a mixed variational formulation of the Stefan-Maxwell equations is found and conditions for well-posedness are determined in the case of ternary diffusion. In the third chapter the ternary mixed variational formulation is discretized using mixed finite element methods. The method is then shown to converge to a solution of the Stefan-Maxwell problem and error estimates between the approximate finite element solution and the exact solution are found. In the fourth chapter, numerical test cases are presented. The first test case is used to verify the error estimates found in chapter three and to be used for comparison to standard methods. Numerical solutions are then found using mixed finite element methods for two other test cases and are compared to solutions obtained with other methods.

Chapter 2

Mixed Variational Formulation of Stefan-Maxwell Equations

In this chapter a mixed variational formulation will be proposed to obtain a weak solution to the Stefan-Maxwell equations. After the problem is set up, the existence of a solution for a linearized problem will be analyzed using standard theory for abstract saddle point problems.

2.1 Variational Formulation

We first establish a mixed variational formulation of the Stefan Maxwell equations given in equations (1.1.1)-(1.1.6).

By looking at the equations we can see that the Stefan-Maxwell equations form a degenerate system. The degeneracy can be removed if equations (1.1.3) and (1.1.4) are used to reduce the system to $n - 1$ species. For $i = 1, 2, \dots, n - 1$, we can do the reduction as follows:

$$-\nabla \xi_i = \frac{1}{c_{tot}} \sum_{j=1}^{n-1} \left(\frac{\xi_j J_i - \xi_i J_j}{D_{ij}} \right) + \frac{\xi_n J_i - \xi_i J_n}{c_{tot} D_{in}}$$

$$\begin{aligned}
&= \sum_{j=1}^{n-1} \left(\frac{\xi_j J_i - \xi_i J_j}{c_{tot} D_{ij}} \right) + \frac{(1 - \xi_1 - \xi_2 - \dots - \xi_{n-1}) J_i + \xi_i (J_1 + J_2 + \dots + J_{n-1})}{c_{tot} D_{in}} \\
&= \frac{J_i}{c_{tot} D_{in}} + \frac{1}{c_{tot}} \sum_{j=1}^{n-1} \left(\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right) (\xi_j J_i - \xi_i J_j)
\end{aligned}$$

Define the following coefficients for $i, j = 1, 2, \dots, n-1$:

$$\alpha_{ij} = \frac{1}{D_{in}} - \frac{1}{D_{ij}}. \quad (2.1.1)$$

The above equation can be stated as:

$$-\nabla \xi_i = \frac{J_i}{c_{tot} D_{in}} + \frac{1}{c_{tot}} \sum_{j=1}^{n-1} \alpha_{ij} (\xi_i J_j - \xi_j J_i) \quad (2.1.2)$$

The molar fraction variable, now defined as $\xi = (\xi_1, \dots, \xi_{n-1})$, is taken to be in $(L^2(\Omega))^{n-1}$. For the rest of the thesis we will use the following definition:

$$V := (L^2(\Omega))^{n-1}. \quad (2.1.3)$$

Before we derive the weak formulation, some preliminary spaces will be defined. To enforce the boundary condition on Γ_N , we need to ensure that it is possible to define an operator which outputs the normal component of a vectorial function on the boundary. This will allow us to embed the boundary condition into the functional space to which J belongs.

To start, we define the trace operator:

Theorem 2.1.1. (*[20], page 10*) *Let Ω be an open bounded set of \mathbb{R}^N with Lipschitz continuous boundary Γ , and let $s > 1/2$. There exists a unique linear continuous map γ , called the trace operator:*

$$\gamma : H^s(\Omega) \rightarrow H^{s-1/2}(\Omega),$$

such that,

$$\gamma(q) := q|_{\Gamma} \quad \forall q \in H^s(\Omega) \cap C^0(\bar{\Omega}).$$

We shall use this trace operator to define a normal trace operator.

Theorem 2.1.2. ([20], page 10) *Let Ω be an open bounded set with a Lipschitz boundary Γ . Then there exists a linear continuous operator $\gamma_\nu \in \mathcal{L}(H(\text{div}; \Omega), H^{-1/2}(\Gamma))$ such that*

$$\gamma_\nu(q) := q \cdot \nu|_\Gamma \quad \forall q \in C^\infty(\overline{\Omega}). \quad (2.1.4)$$

Definition 2.1.3. *Let Ω be Lipschitz domain with boundary Γ and $\Gamma_N \subset \Gamma$. Then the restriction $\gamma_{\nu, \Gamma_N}(q)$ of $\gamma_\nu(q)$ to Γ_N is defined as follows:*

$$\langle \gamma_{\nu, \Gamma_N}(q), \gamma(\Phi) \rangle_{H^{-1/2}(\Gamma_N) \times H^{1/2}(\Gamma_N)} = \langle \gamma_\nu(q), \gamma(\Phi) \rangle_{H^{-1/2}(\Gamma) \times H^{1/2}(\Gamma)}, \quad (2.1.5)$$

for all $\Phi \in H^1(\Omega)$ with $\Phi = 0$ on Γ/Γ_N .

From (2.1.4) we have:

$$\gamma_{\nu, \Gamma_N}(q) = q \cdot \nu|_{\Gamma_N} \quad \forall q \in C^\infty(\overline{\Omega}). \quad (2.1.6)$$

So the flux variable will be taken in the following space:

$$Q = \{q \in (L^2(\Omega))^{n-1} | \nabla \cdot q_i \in L^2(\Omega)\}. \quad (2.1.7)$$

If we enforce boundary conditions on the normal flux we will use the following functional space for J :

$$Q_g = \{q \in (L^2(\Omega))^{n-1} | \nabla \cdot q_i \in L^2(\Omega); \gamma_{\nu, \Gamma_N}(q_i) = g_i \text{ on } \Gamma_N\}, \quad (2.1.8)$$

where $g_i \in H^{-1/2}(\Gamma_N)$ are given for $i = 1, \dots, n-1$. We define Q_0 in a similar fashion where $\gamma_{\nu, \Gamma_N}(q_i) = 0$.

To simplify our notation we write:

$$\langle q \cdot \nu, \Phi \rangle_{\Gamma_N} := \langle \gamma_{\nu, \Gamma_N}(q), \gamma(\Phi) \rangle_{H^{-1/2}(\Gamma_N) \times H^{1/2}(\Gamma_N)}, \quad (2.1.9)$$

and similarly on Γ and Γ_D .

To put these equations into a variational form, we multiply (2.1.2) by a test function q_i , where $q = (q_1, \dots, q_{n-1}) \in Q_0$, and multiply the reaction equation (1.1.2) by a test function v_i where $v = (v_1, \dots, v_{n-1}) \in V$, then integrate both equations over the domain Ω . For $i = 1, 2, \dots, n-1$ we get:

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

By applying integration by parts, the gradient term on each ξ_i can be removed at the cost of a term on the boundary:

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

Since the test function q_i is in the space Q_0 the boundary term vanishes on Γ_N . This leaves the following equations for $i = 1, 2, \dots, n-1$:

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

To enforce the condition on Γ_D we substitute ξ_i with f_i in the boundary term. To ensure the duality product is well defined, f_i will be taken in $H^{1/2}(\Gamma_D)$. We are left with the following mixed variational formulation: Given $f_i \in H^{1/2}(\Gamma_D)$ and $r_i \in L^2(\Omega)$ find $(J, \xi) \in Q_g \times V$ such that:

$$\int_{\Omega} \left(\frac{J_i \cdot q_i}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_i J_j \cdot q_i - \xi_j J_i \cdot q_i) - \xi_i \nabla \cdot q_i \right) dx = - \langle q_i \cdot \nu, f_i \rangle_{\Gamma_D}, \quad (2.1.10)$$

$$\int_{\Omega} v_i \nabla \cdot J_i \, dx = \int_{\Omega} r_i v_i \, dx, \quad (2.1.11)$$

for $i = 1, 2, \dots, n-1$ and $\forall q = (q_1, q_2, \dots, q_{n-1}) \in Q_0$, $\forall v = (v_1, v_2, \dots, v_{n-1}) \in V$.

It will be useful to know what conditions ensure that a solution to the variational formulation is also a solution to the Stefan-Maxwell equations. We will make use of $D(\Omega)$, the space of infinitely differentiable functions with compact support on Ω . Now let $(J, \xi) \in Q_g \times V$ be a solution to the above mixed variational formulation. By rearranging (2.1.11) in the formulation 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 Ω .

To recover the rest of the Stefan-Maxwell problem we consider:

$$\int_{\Omega} \left(\frac{J_i \cdot q_i}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_i J_j \cdot q_i - \xi_j J_i \cdot q_i) - \xi_i \nabla \cdot q_i \right) dx + \langle q_i \cdot \nu, f_i \rangle_{\Gamma_D} = 0.$$

If we assume that $\xi_i \in H^1(\Omega)$ then we can apply integration by parts to the $\xi_i \nabla \cdot q_i$ term and get:

$$\begin{aligned} 0 &= \int_{\Omega} \left(\frac{J_i \cdot q_i}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_i J_j \cdot q_i - \xi_j J_i \cdot q_i) + \nabla \xi_i \cdot q_i \right) dx \\ &\quad - \langle q_i \cdot \nu, \xi_i \rangle_{\Gamma} + \langle q_i \cdot \nu, f_i \rangle_{\Gamma_D} \\ &= \int_{\Omega} \left(\frac{J_i}{c_{tot} D_{in}} + \sum_{j=1}^{n-1} \frac{\alpha_{ij}}{c_{tot}} (\xi_i J_j - \xi_j J_i) + \nabla \xi_i \right) \cdot q_i \, dx \\ &\quad - \langle q_i \cdot \nu, \xi_i \rangle_{\Gamma_N} + \langle q_i \cdot \nu, f_i - \xi_i \rangle_{\Gamma_D} \end{aligned}$$

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 Γ we recover equation (2.1.2) in the sense of distributions. To recover the boundary conditions, take q_i equal to zero on Γ_N . This choice

of q_i is possible due to the surjectivity of the γ_{ν, Γ_N} operator. For this choice of q_i we obtain that:

$$\langle q_i \cdot \nu, f_i - \xi_i \rangle_{\Gamma_D} = 0 \quad \forall q \cdot \nu \in H^{-1/2}(\Gamma_D),$$

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 Γ_D . The boundary condition on the normal flux of J is satisfied in $H^{-1/2}(\Gamma_N)$ since it belongs to Q_g .

So a solution to the mixed variational formulation with $\xi \in (H^1(\Omega))^2$ and $J_i \in H(\text{div}; \Omega)$, will also be a solution to the Stefan-Maxwell problem.

2.2 Existence and Uniqueness for the Linearized Ternary Stefan-Maxwell Equations

In this section the Stefan-Maxwell problem is analyzed using the theory for mixed variational formulations, often referred to as abstract saddle point problems. This theory will be briefly reviewed here, and is based on [7, Ch. II]. Following this review, the general theory will be applied to the case of ternary diffusion.

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 $a(\cdot, \cdot) : Q \times Q \rightarrow \mathbb{R}$ and $b(\cdot, \cdot) : Q \times V \rightarrow \mathbb{R}$. 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:

$$a(J, q) + b(q, \xi) = \langle f, q \rangle_{Q^* \times Q} \quad \forall q \text{ in } Q, \tag{2.2.1}$$

$$b(J, v) = \langle r, v \rangle_{V^* \times V}, \quad \forall v \text{ in } V, \tag{2.2.2}$$

where V^* and Q^* are taken to be the dual spaces of V and Q with $\langle \cdot, \cdot \rangle$ denoting the duality product between the subscripted spaces. The saddle point formulation can be

given in an equivalent operator form by defining operators $A : Q \rightarrow Q^*$, $B : Q \rightarrow V^*$, and $B^* : V \rightarrow Q^*$ such that :

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

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

$$\begin{aligned} AJ + B^*\xi &= f \quad \text{in } Q^*, \\ BJ &= r \quad \text{in } V^*. \end{aligned}$$

To ensure the existence of a solution to the above saddle point problem we make use of the following theorem from page [7, p.42]; where in our case q is the primal variable and v the dual variable:

Theorem 2.2.1. *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 $\text{Ker}(B)$:*

$$a(p, p) \geq \lambda \|p\|_Q^2 > 0 \quad \forall p \in \text{Ker}(B). \quad (2.2.3)$$

- *The bilinear form $b(\cdot, \cdot)$ satisfies the inf-sup condition:*

$$\inf_{v \in V \setminus \text{Ker}(B^*)} \sup_{q \in Q} \frac{b(q, v)}{\|q\|_Q \|v\|_V} \geq \mu > 0 \quad (2.2.4)$$

Then for any $f \in V^*$ and $r \in \text{Im}(B)$, the saddle point problem equations (2.2.1)-(2.2.2) 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 $\text{Ker}(B^*)$.

Proof: For a proof see [7, Ch.II]. ■

To apply Theorem 2.2.1 to the Stefan-Maxwell equations, the nonlinearity will have to be dealt with in some way. In this work the variable ξ_i is taken to be a known non-negative function whenever it is multiplied by a flux J_j . These known functions will be denoted by $\bar{\xi}_i$ and used in a fixed point iteration to solve the fully nonlinear Stefan-Maxwell equations. Additionally we take $c_{tot} \in C(\bar{\Omega})$.

For simplicity we consider the case of ternary diffusion:

$$-\nabla \xi_i = \frac{J_i}{c_{tot} D_{in}} + \frac{1}{c_{tot}} \left(\alpha_{i1} (\xi_i J_1 - \xi_1 J_i) + \alpha_{i2} (\xi_i J_2 - \xi_2 J_i) \right),$$

for $i = 1, 2$, where $\alpha_{ij} = \frac{1}{D_{in}} - \frac{1}{D_{ij}}$.

Since there are only three binary diffusion coefficients, we can always ensure that D_{12} is the largest, by relabeling the three species. Therefore the analysis will assume that this has already been done and D_{12} is in fact the largest of the three binary diffusion coefficients. Define the following quantities:

$$\tilde{\alpha}_1 = \frac{1}{D_{13}} - \alpha_{12} \bar{\xi}_2, \tag{2.2.5}$$

$$\tilde{\alpha}_2 = \alpha_{12} \bar{\xi}_1, \tag{2.2.6}$$

$$\tilde{\beta}_1 = \alpha_{21} \bar{\xi}_2, \tag{2.2.7}$$

$$\tilde{\beta}_2 = \frac{1}{D_{23}} - \alpha_{21} \bar{\xi}_1, \tag{2.2.8}$$

where $\bar{\xi}_1$ and $\bar{\xi}_2$ are assumed to be known non-negative molar fractions in as required for the linearization. The molar fractions $\bar{\xi}_1$ and $\bar{\xi}_2$ will be taken in $L^\infty(\Omega)$ to ensure the continuity of the bilinear form $a(\cdot, \cdot)$.

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

$$a(p, q) = \int_{\Omega} \frac{1}{c_{tot}} \left(\tilde{\alpha}_1 p_1 \cdot q_1 \, dx + \tilde{\alpha}_2 p_2 \cdot q_1 + \tilde{\beta}_1 p_1 \cdot q_2 + \tilde{\beta}_2 p_2 \cdot q_2 \right) dx \quad (2.2.9)$$

$$b(q, v) = - \int_{\Omega} (v_1 \nabla \cdot q_1 + v_2 \nabla \cdot q_2) \, dx. \quad (2.2.10)$$

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

$$a(J, q) + b(q, \xi) = - \langle q \cdot \nu, f \rangle_{\Gamma_D} \quad \forall q \in Q_0, \quad (2.2.11)$$

$$b(J, v) = - \int_{\Omega} r \cdot v \, dx \quad \forall v \in V, \quad (2.2.12)$$

where $r = (r_1, r_2) \in V$.

In order to apply Theorem 2.2.1, the unknowns J and ξ must lie in Hilbert spaces. In general, the zero function is not an element of Q_g , so Q_g is not a Hilbert space. Fortunately this problem can be resolved by letting $J = J_0 + J_g$ where $J_0 \in Q_0$ and $J_g \in Q_g$. This splitting is possible since γ_{ν, Γ_N} is surjective on $H^{-1/2}(\Omega)$. So for any g there will exist a J_g , not necessarily unique, to perform the splitting. Now substituting the definition of J into $a(\cdot, \cdot)$ we get:

$$\begin{aligned} a(J, q) + b(q, \xi) &= - \langle f, q \rangle_{\Gamma_D} \\ a(J_0 + J_g, q) + b(q, \xi) &= - \langle f, q \rangle_{\Gamma_D} \\ a(J_0, q) + a(J_g, q) + b(q, \xi) &= - \langle f, q \rangle_{\Gamma_D} \\ a(J_0, q) + b(q, \xi) &= - \langle f, q \rangle_{\Gamma_D} - a(J_g, q) \end{aligned}$$

Repeating this process with $b(\cdot, \cdot)$:

$$b(J, v) = -(r, v)_V$$

$$\begin{aligned} b(J_0 + J_g, v) &= -(r, v)_V \\ b(J_0, v) + b(J_g, v) &= -(r, v)_V \\ b(J_0, v) &= -(r, v)_V - b(J_g, v) \end{aligned}$$

Define two linear functionals as follows

$$\langle \tilde{f}, q \rangle_{Q^* \times Q} = - \langle f, q \rangle_{\Gamma_D} - a(J_g, q), \quad (2.2.13)$$

and

$$\langle \tilde{r}, v \rangle_{V^* \times V} = -(r, v)_V - b(J_g, v), \quad (2.2.14)$$

The problem can now be restated: Find $(J, \xi) \in Q_0 \times V$ such that:

$$a(J, q) + b(q, \xi) = \langle \tilde{f}, q \rangle_{Q^* \times Q}, \quad \forall q \in Q_0, \quad (2.2.15)$$

$$b(J, v) = \langle \tilde{r}, v \rangle_{V^* \times V}, \quad \forall v \in V. \quad (2.2.16)$$

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 2.2.1.

To start, consider the following lemma:

Lemma 2.2.2. *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 $\tilde{\beta}_2 - \tilde{\beta}_1 \geq \frac{1}{D_{12}}$.*

Proof:

We first prove that $\tilde{\alpha}_1 - \tilde{\alpha}_2 \geq \frac{1}{D_{12}}$.

$$\begin{aligned} \tilde{\alpha}_1 - \tilde{\alpha}_2 &= \frac{1}{D_{13}} - \left(\frac{1}{D_{13}} - \frac{1}{D_{12}}\right)\bar{\xi}_1 - \left(\frac{1}{D_{13}} - \frac{1}{D_{12}}\right)\bar{\xi}_2 \\ &= \frac{1 - \bar{\xi}_1}{D_{13}} + \frac{\bar{\xi}_1}{D_{12}} - \frac{\bar{\xi}_2}{D_{13}} + \frac{\bar{\xi}_2}{D_{12}} \\ &= \frac{1 - \bar{\xi}_1 - \bar{\xi}_2}{D_{13}} + \frac{\bar{\xi}_1 + \bar{\xi}_2}{D_{12}} \end{aligned}$$

$$\begin{aligned}
&\geq \frac{1 - \bar{\xi}_1 - \bar{\xi}_2}{D_{12}} + \frac{\bar{\xi}_1 + \bar{\xi}_2}{D_{12}} \\
&= \frac{1}{D_{12}}
\end{aligned}$$

Now to prove the other inequality, we proceed in much the same way:

$$\begin{aligned}
\tilde{\beta}_2 - \tilde{\beta}_1 &= \frac{1}{D_{23}} - \left(\frac{1}{D_{23}} - \frac{1}{D_{12}}\right)\bar{\xi}_2 - \left(\frac{1}{D_{23}} - \frac{1}{D_{12}}\right)\bar{\xi}_1 \\
&= \frac{1 - \bar{\xi}_2}{D_{23}} + \frac{\bar{\xi}_2}{D_{12}} - \frac{\bar{\xi}_1}{D_{23}} + \frac{\bar{\xi}_1}{D_{12}} \\
&= \frac{1 - \bar{\xi}_1 - \bar{\xi}_2}{D_{23}} + \frac{\bar{\xi}_1 + \bar{\xi}_2}{D_{12}} \\
&\geq \frac{1 - \bar{\xi}_1 - \bar{\xi}_2}{D_{12}} + \frac{\bar{\xi}_1 + \bar{\xi}_2}{D_{12}} \\
&= \frac{1}{D_{12}}
\end{aligned}$$

We have used the fact that the $\bar{\xi}_i$'s add up to one and that the binary diffusion coefficient D_{12} is the largest. ■

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

Proposition 2.2.3. *If the binary diffusion coefficients satisfy $3D_{23} > D_{12}$ and $3D_{13} > D_{12}$, then the bilinear form $a(\cdot, \cdot)$ is coercive and continuous.*

Proof: We rewrite the bilinear form in the following way:

$$a(p, q) = \int_{\Omega} \frac{1}{c_{tot}} \sum_{i=1}^2 (q_1^i, q_2^i) \begin{pmatrix} \tilde{\alpha}_1 & \tilde{\alpha}_2 \\ \tilde{\beta}_1 & \tilde{\beta}_2 \end{pmatrix} \begin{pmatrix} p_1^i \\ p_2^i \end{pmatrix} dx$$

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

To start we consider the coercivity of $a(\cdot, \cdot)$. 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 $\bar{\xi}_i$. So to prove the coercivity we will consider:

$$A_{sym} = \begin{pmatrix} \tilde{\alpha}_1 & \frac{\tilde{\alpha}_2 + \tilde{\beta}_1}{2} \\ \frac{\tilde{\alpha}_2 + \tilde{\beta}_1}{2} & \tilde{\beta}_2 \end{pmatrix}.$$

Positive definiteness of the matrix will be established by showing that the matrix has strictly positive eigenvalues. To do this we apply the Gershgorin circle theorem to find lower bounds on the eigenvalues of A_{sym} .

We now consider the Gershgorin circle for the first row:

$$\begin{aligned} 2\tilde{\alpha}_1 - (\tilde{\alpha}_2 + \tilde{\beta}_1) &\geq 2\tilde{\alpha}_1 - \left(\tilde{\alpha}_1 - \frac{1}{D_{12}} + \tilde{\beta}_1\right) \\ &= \frac{1}{D_{13}} - \alpha_{12}\bar{\xi}_2 - \alpha_{21}\bar{\xi}_2 + \frac{1}{D_{12}} \\ &= \frac{1}{D_{13}} - \left(\frac{1}{D_{13}} - \frac{1}{D_{12}}\right)\bar{\xi}_2 - \left(\frac{1}{D_{23}} - \frac{1}{D_{12}}\right)\bar{\xi}_2 + \frac{1}{D_{12}} \\ &= \frac{1 - \bar{\xi}_2}{D_{13}} + 2\frac{\bar{\xi}_2}{D_{12}} - \frac{\bar{\xi}_2}{D_{23}} + \frac{1}{D_{12}} \end{aligned}$$

where the inequality comes from applying Lemma 2.2.2.

This last line is a linear equation in $\bar{\xi}_2$, so for $\bar{\xi}_2 \in [0, 1]$ 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 $3D_{23} > D_{12}$.

Now consider the other Gershgorin circle:

$$2\tilde{\beta}_2 - (\tilde{\alpha}_2 + \tilde{\beta}_1) \geq 2\tilde{\beta}_2 - \left(\tilde{\alpha}_2 + \tilde{\beta}_2 - \frac{1}{D_{12}}\right)$$

$$\begin{aligned}
&= \frac{1}{D_{23}} - \alpha_{21}\bar{\xi}_1 - \alpha_{12}\bar{\xi}_1 + \frac{1}{D_{12}} \\
&= \frac{1}{D_{23}} - \left(\frac{1}{D_{23}} - \frac{1}{D_{12}}\right)\bar{\xi}_1 - \left(\frac{1}{D_{13}} - \frac{1}{D_{12}}\right)\bar{\xi}_1 + \frac{1}{D_{12}} \\
&= \frac{1 - \bar{\xi}_1}{D_{23}} + 2\frac{\bar{\xi}_1}{D_{12}} - \frac{\bar{\xi}_1}{D_{13}} + \frac{1}{D_{12}}.
\end{aligned}$$

As before the last line is a linear equation in $\bar{\xi}_1$. So we get:

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

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 in fact positive definite.

To prove the continuity of $a(\cdot, \cdot)$ we only need to show that the operator A is bounded [2, pg. 334]. Therefore we need to show that $\|Av\|_{V^*} \leq C\|v\|_{V^*}$. By showing that the matrix A_{sym} has uniformly bounded coefficients, we obtain that the constant C in this inequality is finite. Since $\bar{\xi}_i \in [0, 1]$ the functions $\tilde{\alpha}_i$ and $\tilde{\beta}_i$ are bounded above by $\frac{1}{D_{13}}$ and $\frac{1}{D_{23}}$ respectively. By taking $C = \max\{\frac{1}{D_{13}}, \frac{1}{D_{23}}\}$ we get that $\|Av\|_{V^*} \leq C\|v\|_{V^*}$. Therefore we can conclude that $a(p, q)$ is continuous. ■

To prove the inf-sup condition for $b(\cdot, \cdot)$ we will make use of the following lemma from [20]:

Lemma 2.2.4. *For any $v \in L^2(\Omega)$ there exists $p \in H(\text{div}; \Omega)$ such that $\nabla \cdot p = -v$ and that satisfies the following inequality:*

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

where C_Ω is the constant in the Poincaré inequality for the domain Ω .

Proof: For a given $v \in L^2(\Omega)$ consider the following variational problem: Find $\phi \in H_0^1(\Omega)$ such that:

$$\int_{\Omega} \nabla \phi \cdot \nabla \psi \, dx = \int_{\Omega} v \psi \, dx \quad \forall \psi \in H_0^1(\Omega).$$

By the Lax-Milgram theorem for any $v \in L^2(\Omega)$ there exists a unique $\phi \in H_0^1(\Omega)$ which satisfies the above variational equation. By taking the test function ψ equal to ϕ , we get:

$$\begin{aligned} \|\nabla \phi\|_{L^2(\Omega)}^2 &= \int_{\Omega} |\nabla \phi|^2 \, dx \\ &= \int_{\Omega} v \phi \, dx \\ &\leq \|v\|_{L^2(\Omega)} \|\phi\|_{L^2(\Omega)} \\ &\leq C_{\Omega} \|v\|_{L^2(\Omega)} \|\nabla \phi\|_{L^2(\Omega)} \\ \implies \|\nabla \phi\|_{L^2(\Omega)} &\leq C_{\Omega} \|v\|_{L^2(\Omega)} \end{aligned}$$

Setting $p = \nabla \phi$ and integrating by parts:

$$\begin{aligned} \int_{\Omega} v \psi \, dx &= \int_{\Omega} p \cdot \nabla \psi \, dx \\ &= \langle p \cdot \nu, \psi \rangle_{\Gamma} - \int_{\Omega} \psi \nabla \cdot p \, dx \\ &= - \int_{\Omega} \psi \nabla \cdot p \, dx, \end{aligned}$$

where the boundary term vanishes because $\psi = 0$ on Γ . Take $\psi \in D(\Omega) \subset H_0^1(\Omega)$, we get that $\nabla \cdot p = -v$ in $D'(\Omega)$. Combining the above results we get the following:

$$\begin{aligned} \|p\|_{H(\text{div}; \Omega)}^2 &= \|p\|_{L^2(\Omega)}^2 + \|\nabla \cdot p\|_{L^2(\Omega)}^2 \\ &\leq \|\nabla \phi\|_{L^2(\Omega)}^2 + \|\nabla \cdot p\|_{L^2(\Omega)}^2 \end{aligned}$$

$$= C_\Omega^2 \|v\|_{L^2(\Omega)}^2 + \|v\|_{L^2(\Omega)}^2,$$

which immediately implies the desired result. ■

We can now prove the following proposition:

Proposition 2.2.5. *The bilinear form $b(\cdot, \cdot)$ for the Stefan-Maxwell 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 v_1 and v_2 be $L^2(\Omega)$ functions such that $\nabla \cdot p_i = v_i$, $i = 1, 2$, as in Lemma 2.2.4. Then we have:

$$\begin{aligned} b(p, v) &= \frac{\int_\Omega -v_1 \nabla \cdot p_1 - v_2 \nabla \cdot p_2 \, dx}{\|[v_1, v_2]\|_V} \\ &= \frac{\|v_1\|_{L^2(\Omega)}^2 + \|v_2\|_{L^2(\Omega)}^2}{\sqrt{\|v_1\|_{L^2(\Omega)}^2 + \|v_2\|_{L^2(\Omega)}^2}} \\ &= \sqrt{\|v_1\|_{L^2(\Omega)}^2 + \|v_2\|_{L^2(\Omega)}^2} \\ &\geq \sqrt{\left(\|p_1\|_{H(\text{div}; \Omega)}^2 + \|p_2\|_{H(\text{div}; \Omega)}^2\right)} \frac{1}{1 + C_\Omega^2} \\ &= \frac{1}{\sqrt{1 + C_\Omega^2}} \|p\|_Q, \end{aligned}$$

where the inequality comes from Lemma 2.2.4. This leads to the following:

$$\sup_{p \in Q} \frac{b(p, v)}{\|p\|_Q} \geq \frac{\int_\Omega -v_1 \nabla \cdot p_1 - v_2 \nabla \cdot p_2 \, dx}{\|p\|_Q}$$

$$\geq \frac{1}{\sqrt{1+C_\Omega^2}} \|v\|_V$$

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

We can use the results in this section to prove the following theorem:

Theorem 2.2.6. *There exists a unique solution $(J, \xi) \in Q_g \times V$ to the mixed formulation of the linearized Stefan-Maxwell equations, when the binary diffusion coefficients satisfy $3D_{23} > D_{12}$ and $3D_{13} > D_{12}$.*

Proof: By the application of Theorem 2.2.1 we have that there exists a solution $(J, \xi) \in Q_g \times V$ to the Stefan-Maxwell problem. Furthermore if $J = J_0 + J_g$, then J_0 will be defined uniquely for a given J_g . Now consider two solutions to the Stefan-Maxwell problem, (J^1, ξ^1) and (J^2, ξ^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 Γ_N and $\tilde{\xi} = 0$ on Γ_D . So $(\tilde{J}, \tilde{\xi}) \in Q_0 \times V$ is a solution to:

$$\begin{aligned} a(\tilde{J}, q) + b(q, \tilde{\xi}) &= 0 \quad , \forall q \in Q_0, \\ b(\tilde{J}, v) &= 0 \quad , \forall v \in V. \end{aligned}$$

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:

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

Set $q_i \in (D(\Omega))^d \subset H(\text{div}; \Omega)$. Then 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 ξ_i is $L^2(\Omega)$ we have that ξ_i coincides almost everywhere with a constant function [5, Corollary 2.1, p.9]. Since ξ is a constant function we have that $\xi_i \in H^1(\Omega)$. Now for $q_i \in Q_0$ we get:

$$\begin{aligned} 0 &= \int_{\Omega} \tilde{\xi}_i \nabla \cdot q_i \, dx \\ &= - \int_{\Omega} \nabla \tilde{\xi}_i \cdot q_i \, dx + \langle q_i \cdot \nu, \tilde{\xi}_i \rangle_{\Gamma} \\ &= \langle q_i \cdot \nu, \tilde{\xi}_i \rangle_{\Gamma_D}, \end{aligned}$$

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 Ω .

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

Remark: In order to consider the fully nonlinear Stefan-Maxwell equations we would need to consider a fixed point mapping from $\bar{\xi}_i$ to ξ_i and show that it converges in some space. This was attempted using Sobolev embeddings, in particular the Rellich-Kondrachov Theorem. However we were unable to make any progress as the fixed point mapping was continuous but not compact.

Chapter 3

Numerical Analysis

The theory of mixed finite element methods is summarized here with an emphasis on results that will be used to approximate the Stefan-Maxwell problem. In the first section the general mixed finite element problem is stated as well as the main theorem for solution existence. In the second section the finite element spaces that approximate the functional spaces of the continuous problem are stated. The final section investigates the stability and the order of convergence for different finite element spaces.

3.1 Discretization of Stefan-Maxwell Equation

The finite dimensional approximation of the Stefan-Maxwell problem (2.2.15)-(2.2.16) is as follows: Find $(J_h, \xi_h) \in Q_h \times V_h$ that satisfy the following:

$$a(J_h, q_h) + b(q_h, \xi_h) = \langle f, q_h \rangle_{Q^*, Q} \quad \forall q_h \in Q_h, \quad (3.1.1)$$

$$b(J_h, v_h) = \langle r, v_h \rangle_{V^*, V} \quad \forall v_h \in V_h, \quad (3.1.2)$$

where V_h and Q_h are finite dimensional subspaces of V and Q , respectively. The bilinear forms above define two operators, $A_h : Q_h \rightarrow Q_h^*$ and $B_h : Q_h \rightarrow V_h^*$. The

operator B_h has a kernel defined as $Ker(B_h) = \{q_h \in Q_h \mid B_h q_h = 0\} = \{q_h \in Q_h \mid b(q_h, v_h) = 0, \forall v_h \in V_h\}$.

The existence of a solution for the continuous problem does not imply the existence of a solution to the discrete problem. This is because, in general, the operator B_h is not the restriction of B to Q_h .

The existence of a solution for the mixed finite element method is established by the following theorem from [7, p.60]:

Theorem 3.1.1. *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 λ_h and μ_h :

(i) The bilinear form $a(\cdot, \cdot)|_{V_h \times V_h}$ satisfies the following coercivity condition on $Ker(B_h)$:

$$a(p_h, p_h) \geq \lambda_h \|p_h\|_Q^2 > 0 \quad \forall p_h \in Ker(B_h). \quad (3.1.3)$$

(ii) The bilinear form $b(\cdot, \cdot)|_{V_h \times Q_h}$ satisfies the following inf-sup condition:

$$\inf_{v_h \in V_h \setminus Ker(B_h^*)} \sup_{q_h \in Q_h} \frac{b(q_h, v_h)}{\|q_h\|_Q \|v_h\|_V} \geq \mu_h > 0. \quad (3.1.4)$$

Then for any $f \in Q^$ and $r \in Im(B)$ 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 ξ_h is unique up to an element of $Ker(B_h^*)$.*

Proof:

Full proof can be found in [7, section 2.2].

■

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:

$$\|J - J_h\|_Q \leq \left(1 + \frac{\|a\|}{\lambda}\right) \left(1 + \frac{\|b\|}{\mu}\right) \inf_{q_h \in Q_h} \|J - q_h\|_Q + \frac{\|b\|}{\lambda} \inf_{v_h \in V_h} \|\xi - v_h\|_V, \quad (3.1.5)$$

$$\|\xi - \xi_h\|_V \leq \left(1 + \frac{\|b\|}{\mu}\right) \inf_{v_h \in V_h} \|\xi - v_h\|_V + \frac{\|a\|}{\mu} \inf_{q_h \in Q_h} \|J - q_h\|_Q. \quad (3.1.6)$$

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

$$\|J - J_h\|_Q \leq \left(1 + \frac{\|a\|}{\lambda}\right) \left(1 + \frac{\|b\|}{\mu}\right) \inf_{q_h \in Q_h} \|J - q_h\|_Q. \quad (3.1.7)$$

A proof of these error estimates and others can be found in [7, Sec 2.2].

3.2 Finite Element Spaces

In order to determine if a specific mixed finite element method satisfies the hypothesis of Theorem 3.1.1, two finite dimensional approximations of the spaces V and Q need to be specified on any mesh T_h . For this paper the mesh T_h will always be a regular triangular mesh. This means that the domain Ω will be tessellated by triangles, such that if any two triangles share an edge, then they share the entire edge. Individual triangles in the mesh will be denoted by K . Let $h = \max_{K \in T_h} h_k$, where h_k is the size of the element K .

The space V will be approximated with the finite dimensional space P_{dc}^k of piecewise polynomials of degree k , which are discontinuous on element boundaries. If $\mathbb{P}_k(K)$ is taken to be the space of k -th degree polynomials on any element K , then P_{dc}^k is defined as follows:

$$P_{dc}^k = \{v_h \in (L^2(\Omega))^2 \mid v_h|_K \in (\mathbb{P}_k(K))^2 \forall K \in T_h\} \quad (3.2.1)$$

For $k > 0$, if we enforce continuity across elements K of T_h then we get the following space:

$$P^k = \{v_h \in (C^0(\bar{\Omega}))^2 \mid v_h|_K \in (\mathbb{P}(k))^2 \forall K \in T_h \} \quad (3.2.2)$$

There exists an interpolation operator onto the space P_{dc}^k with the following property from [20, p.90]:

Proposition 3.2.1. *Let k be a nonnegative integer. The interpolation operator $\Pi_h : V \rightarrow P_{dc}^k$ satisfies the following error estimate for $k \geq 0$:*

$$\|v - \Pi_h v\|_V^2 \leq ch^{k+1} |v|_{k+1, \Omega} \quad \forall v \in (H^{k+1}(\Omega))^2, \quad (3.2.3)$$

where $|v|_{k+1, \Omega}$ is the $H^{k+1}(\Omega)$ seminorm.

The space Q will be approximated using the k -th order Raviart-Thomas finite element, RT^k . To construct the space we need the following definition:

Definition 3.2.2. *A homogeneous polynomial is one where all non zero terms have the same degree. The space of homogeneous polynomials of degree k will be denoted by $\tilde{\mathbb{P}}_k$.*

Using homogeneous polynomials we will define the following space on an element K :

$$RT^k(K) = (\mathbb{P}_k(K))^2 + \begin{pmatrix} x \\ y \end{pmatrix} \tilde{\mathbb{P}}_k(K).$$

The degrees of freedom for RT^k are chosen such that the normal component $q_h \cdot \nu$ is continuous across element edges. This is done in such a way as to ensure that the element is a subspace of $H(\text{div}; \Omega)$. For $k = 0$, the degrees of freedom for $q \cdot \nu$ are taken at the mid-edges. For $k \geq 0$, see [7] for details on how this is done. We can

now define the Raviart-Thomas finite element space over the entire domain Ω . For $k \geq 0$:

$$RT^k = \{q_h \in (H(\operatorname{div}; \Omega))^2 \mid q_{h,i}|_K \in RT^k(K), i = 1, 2, \forall K \in T_h\}. \quad (3.2.4)$$

The space $H(\operatorname{div}; \Omega)$ can also be approximated with the Brezzi-Douglas-Marini elements of order $k + 1$ [6]. The space BDM^{k+1} defined by:

$$BDM^{k+1} = \{q_h \in (H(\operatorname{div}; \Omega))^2 \mid q_{h,i}|_K \in (P_{dc}^k(K))^2, i = 1, 2, \forall K \in T_h\}. \quad (3.2.5)$$

The degrees of freedom for BDM^{k+1} finite element functions are chosen such that the functions are in $H(\operatorname{div}; \Omega)$. For triangular elements we have that $RT^0 \subset BDM^1 \subset RT^1 \subset BDM^2$ and so on.

The space RT^k has an interpolation operator, τ_h , with the following property:

Proposition 3.2.3. *Let $v \in P_{dc}^k$. There exists an interpolator $\tau_h : (H(\operatorname{div}; \Omega))^2 \rightarrow RT^k$ that satisfies the following properties:*

$$(i) \int_{\Omega} v_i \nabla \cdot (q_i - \tau_h(q_i)) = 0, \quad (3.2.6)$$

$$(ii) \|\tau_h(q)\|_Q \leq C_* \|q\|_Q, \quad (3.2.7)$$

for a constant C_* independent of h .

The interpolator also satisfies the following error estimate for $q \in (H^{k+1}(\Omega))^2$:

$$\|\tau_h(q) - q\|_Q \leq Ch^{k+1} (\|q\|_{k+1, \Omega} + \sum_{i=1}^2 |\operatorname{div}(q_i)|_{k+1, \Omega}) \quad (3.2.8)$$

Proof: See Sec 3.4.2 and 7.2.2 in [20]. ■

These finite element spaces and their associated properties will be essential in proving that the method converges. The properties of the interpolators will be necessary for investigating the convergence order of the method.

3.3 Stability and Convergence of the Finite Element Method

To analyze the stability and convergence of mixed finite element methods, 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_{dc}^k or the BDM^{k+1}/P_{dc}^k combinations for discretizing J and ξ , respectively. This choice of spaces has the property that $\text{div}(RT^k) = \text{div}(BDM^{k+1}) = P_{dc}^k$. This means that the operator B_h is just the restriction of B to the subspace RT^k or BDM^{k+1} . So the coercivity condition on $a(\cdot, \cdot)$ over $\text{Ker}(B_h)$ is implied by the coercivity condition over $\text{Ker}(B)$. For the rest of the convergence analysis, only the Raviart-Thomas space will be considered, although the BDM^{k+1} analysis is very similar.

Lemma 3.3.1. *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, equation (2.2.4). Now assume there exists an operator $\tau_h : Q \rightarrow RT^k$ such that:*

$$(1) \int_{\Omega} v_h \nabla \cdot (q_i - \tau_h(q_i)) = 0 \quad i = 1, 2, \quad (3.3.1)$$

$$(2) \|\tau_h(q)\|_Q \leq C_* \|q\|_Q, \quad (3.3.2)$$

then the inf-sup condition for the discrete problem (3.1.4) is satisfied for a constant independent of h .

Proof: See [7, Prop. 2.8, p. 58] or [20, Lemma 7.2.1, p. 235]. ■

We can now prove the following proposition:

Proposition 3.3.2. *If $q_i \in H(\text{div}; \Omega)^2$, then the inf-sup condition for the discrete problem (3.1.4) is satisfied for $Q_h = RT^k$ and $V_h = P_{dc}^k$.*

Proof: By Theorem 2.2.1 there exists a μ such that $\forall v \in V, \exists q \in Q, q \neq 0$ that satisfies the continuous inf-sup condition, equation (2.2.4). Since $q_i \in H(\operatorname{div}; \Omega)^2$, by Proposition 3.2.3 there exists an operator $\tau_h : H(\operatorname{div}; \Omega)^2 \rightarrow RT^k$ that satisfies (3.2.5) and (3.2.6). Now we can apply Lemma 3.3.1 and conclude that the inf-sup condition for the discrete problem (3.1.5) is satisfied for a constant independent of h . ■

We will conclude this section with the following theorem:

Theorem 3.3.3. *Assume the binary diffusion coefficients satisfy $3D_{23} > D_{12}$ and $3D_{13} > D_{12}$. The mixed finite element method for the linearized Stefan-Maxwell problem defined by (3.1.1)-(3.1.2) has a solution $(J_h, \xi_h) \in RT^k \times P_{dc}^k$, where J_h and ξ_h are unique. Provided the solution $(\xi, J) \in (H^{k+1}(\Omega))^2 \times (H^{k+1}(\Omega))^2$, then the following error estimates are satisfied:*

$$\|\xi - \xi_h\|_V \leq Ch^{k+1}(\|\xi\|_{k+1,\Omega} + |J|_{k+1,\Omega} + |\operatorname{div}(J)|_{k+1,\Omega}), \quad (3.3.3)$$

$$\|J - J_h\|_V \leq Ch^{k+1}(|J|_{k+1,\Omega} + |\operatorname{div}(J)|_{k+1,\Omega}), \quad (3.3.4)$$

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

Proof: By proposition 3.3.2 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 $(H(\operatorname{div}; \Omega))^2$. Therefore by Theorem 3.1.1 we have the existence of a solution $(J_h, \xi_h) \in RT^k \times P_{dc}^k$.

Since $\operatorname{Ker}(B_h) \subset \operatorname{Ker}(B)$ we have the following error estimates from (3.1.6) and (3.1.7):

$$\|\xi - \xi_h\|_V \leq c_1 \inf_{v_h \in P_{dc}^k} \|\xi - v_h\|_V + c_2 \inf_{q_h \in RT^k} \|J - q_h\|_Q,$$

$$\|J - J_h\|_V \leq c_3 \inf_{q_h \in RT^k} \|J - q_h\|_Q,$$

where $c_1 = (1 + \frac{\|b\|}{\mu})$, $c_2 = \frac{\|a\|}{\mu}$, and $c_3 = (1 + \frac{\|a\|}{\lambda})(1 + \frac{\|b\|}{\mu})$.

We use the interpolation operator's error estimate, (3.2.3), to get an error estimate for ξ in terms of semi-norms.

$$\begin{aligned} \inf_{v_h \in P_{dc}^k} \|\xi - v_h\|_V &\leq \|\xi - \Pi_h \xi\|_V \\ &\leq ch^{k+1} |\xi|_{k+1, \Omega} \quad \forall \xi \in (H^{k+1}(\Omega))^2, \end{aligned}$$

with a constant c independent from h and ξ .

We proceed in the same way using the interpolator (3.2.7) to get an error estimate for J in terms of the H^{k+1} seminorm.

$$\begin{aligned} \inf_{q_h \in RT^k} \|J - q_h\|_Q &\leq \|J - \tau_h J\|_Q \\ &\leq Ch^{k+1} (|J|_{k+1, \Omega} + |\operatorname{div}(J)|_{k+1, \Omega}), \end{aligned}$$

where this holds for all $\forall J \in (H^{k+1}(\Omega))^2$. We can now substitute the estimates for the infimums of the norms into the error estimates above to get equations (3.3.3) and (3.3.4). ■

3.4 Standard Finite Element Methods

For the sake of completeness standard finite element methods are presented here. For this, we make use of the following definition:

$$A = \begin{pmatrix} \tilde{\alpha}_1 & \tilde{\alpha}_2 \\ \tilde{\beta}_1 & \tilde{\beta}_2 \end{pmatrix}$$

where the terms in the matrix are defined by equations (2.2.5)-(2.2.8).

By taking equation (1.1.1) and using equations (1.1.3) and (1.1.4), the three species system is reduced to the following two species system:

$$-\nabla \xi_i = \sum_{j=1}^2 A_{ij} J_j,$$

for $i = 1, 2$.

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

$$J_i = - \sum_{j=1}^2 A_{ij}^{-1} \nabla \xi_j, \quad (3.4.1)$$

for $i = 1, 2$.

By taking the divergence on both sides and applying equation (1.1.2), we obtain the following for $i = 1, 2$:

$$-\nabla \cdot \left(\sum_{j=1}^2 A_{ij}^{-1} \nabla \xi_j \right) = r_i.$$

The variational formulation is obtained by multiplying the above by a test function ϕ_i and integrating by parts to remove the divergence term. For a Dirichlet problem this yields the following variational formulation: Find $\xi \in (H^1(\Omega))^2$ where $\xi_i = f_i$ on Γ such that:

$$\int_{\Omega} \left(\sum_{j=1}^2 A_{ij}^{-1} \nabla \xi_j \right) \cdot \nabla \phi_i \, dx = \int_{\Omega} r_i \phi_i \, dx, \quad (3.4.2)$$

for all $\phi_i \in H_0^1(\Omega)$ and $i = 1, 2$. Just like in the case of the mixed finite element method, this problem is solved multiple times where the nonlinearity is resolved using the fixed point $\bar{\xi}_{h,i} := \sigma \xi_{h,i} + (1 - \sigma) \bar{\xi}_{h,i}$. The finite element space approximation will use the continuous P^k spaces for $k \geq 1$. These finite element methods will be referred to as ‘‘Standard P^k ’’.

For these ‘‘Standard P^k ’’ methods the flux will be recovered by solving (3.4.2) for ξ and using equation (3.4.1) to strongly recover the flux J . The flux component

J_i will be approximated by the space $P^{2k} \times P^{2k}$ for $i = 1, 2$ as this yielded the lowest L^2 error in the numerical tests described in the next chapter.

Chapter 4

Numerical Results

In this chapter the mixed finite element method is used to compute approximate solutions to the Stefan-Maxwell equations. We first discuss the implementation of the mixed finite element method using FreeFem++[13]. Three test cases are considered. The first test case has a known analytic solution which is compared to the mixed finite element solution and used to verify the error estimates from the previous section. The second test case was initially proposed by Mazumder in [17], and its solution is computed using the numerical scheme. The third case, proposed by Bottcher in [4], is a variation of the Mazumder test case.

4.1 Implementation of the Mixed Finite Element Method

The mixed finite element methods were implemented using the open source software FreeFem++[13]. Computations were done using the 64-bit version of Ubuntu 12.10 on a computer with 9GBs of RAM and an Intel Core i7 processor.

The software was used to construct the meshes, to build the finite element functions, and for plotting the solutions.

A fixed point iteration was used to resolve the nonlinearity of the Stefan-Maxwell equations. The $\bar{\xi}_i$ 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 ξ_h was compared to the initial guess $\bar{\xi}_h$ through a computation of $\|\xi_h - \bar{\xi}_h\|_V$. If the norm was greater than 10^{-10} , the functions $\bar{\xi}_{h,i}$ were updated using the following equation:

$$\bar{\xi}_{h,i} = \sigma \xi_{h,i} + (1 - \sigma) \bar{\xi}_{h,i}, \quad (4.1.1)$$

where $\sigma \in [0, 1]$. A σ value less than one represents an under-relaxation of the fixed point and may be necessary to achieve convergence. The procedure is then repeated using the new values for the $\bar{\xi}_i$ functions until the norm $\|\xi_h - \bar{\xi}_h\|_V$ is less than 10^{-10} . The fixed point iterations were then stopped and the solution (J, ξ) was plotted using FreeFEM++'s built in plot function.

4.2 Analytic Test Case

A test case was constructed on a domain Ω with boundary conditions and reaction rates such that the solution to the Stefan-Maxwell 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 Stefan-Maxwell problem is satisfied. Define two functions f_1 and f_2 as follows:

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

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

For this benchmark, Dirichlet boundary conditions are used on all Γ , i.e. $\Gamma_D = \Gamma$.

The reaction rates are defined by two functions r_1 and r_2 in the domain Ω as follows:

$$r_1 = \left(\frac{\alpha_{21}}{\chi} - \frac{\alpha_{21}\tilde{\beta}_2}{D_{12}\chi^2} + \frac{\tilde{\alpha}_2\alpha_{12}}{D_{23}\chi^2} \right) \left(\frac{\sin(\pi x/2) + \sinh(\pi y/2)}{4\pi^2} \right) \quad (4.2.1)$$

$$r_2 = \left(\frac{\alpha_{12}}{\chi} - \frac{\alpha_{12}\tilde{\alpha}_1}{D_{23}\chi^2} + \frac{\tilde{\beta}_1\alpha_{21}}{D_{13}\chi^2} \right) \left(\frac{\sin(\pi x/2) + \sinh(\pi y/2)}{4\pi^2} \right), \quad (4.2.2)$$

where the χ in the above equations is defined as follows:

$$\chi = \frac{1}{D_{13}D_{23}} - \frac{\alpha_{12}\xi_1}{D_{23}} - \frac{\alpha_{21}\xi_2}{D_{13}}. \quad (4.2.3)$$

The exact solution of the Stefan-Maxwell equations for this data is given by:

$$\xi_1 = \frac{\sin(\pi x/2)\sinh(\pi y/2)}{\pi^2}, \quad (4.2.4)$$

$$\xi_2 = \frac{\cos(\pi x/2)\cosh(\pi y/2)}{\pi^2}, \quad (4.2.5)$$

$$J_1 = \frac{-\tilde{\beta}_2}{\chi} \nabla \xi_1 + \frac{\tilde{\alpha}_2}{\chi} \nabla \xi_2, \quad (4.2.6)$$

$$J_2 = \frac{\tilde{\beta}_1}{\chi} \nabla \xi_1 - \frac{\tilde{\alpha}_1}{\chi} \nabla \xi_2. \quad (4.2.7)$$

The problem was then solved using the mixed finite element problem described in the previous section with a uniform triangular mesh, seen in Figure 4.1. The binary

diffusion coefficients were taken to be as follows: $D_{12} = 15$, $D_{13} = 10$, and $D_{23} = 5$. The concentration was taken to be uniform everywhere, $c_{tot} = 1$. The L^2 -errors for the mole fractions (E_ξ) and for the fluxes (E_J) were computed with varying mesh sizes using the three different mixed finite element methods. Using $\sigma = 1$ the fixed point method usually converges in about 6 iterations for this test case. The errors were defined as follows:

$$E_\xi = \left(\int_{\Omega} |\xi_1 - (\xi_1)_h|^2 + |\xi_2 - (\xi_2)_h|^2 dx \right)^{1/2}, \quad (4.2.8)$$

$$E_J = \left(\int_{\Omega} |J_1 - (J_1)_h|^2 + |J_2 - (J_2)_h|^2 dx \right)^{1/2}. \quad (4.2.9)$$

The mixed finite element space combinations are RT^0/P_{dc}^0 , RT^1/P^1 , RT^1/P_{dc}^1 , and BDM^1/P_{dc}^0 where the first element refers to the flux space (Q_h) and the second refers to the molar fraction space (V_h). Note that the space RT^1/P^1 does not fall under the hypothesis of Theorem 3.3.3, hence it is not clear what the expected convergence rate should be in this case. The problem was also solved using standard finite element methods with the finite element spaces P^1 and P^2 .

Figure 4.2 shows plots of $-\ln(E)$ as a function of $-\ln(h)$ for all methods. A linear best fit was found using the least squares method, so that the slope of the lines could be used to determine the order of convergence for each method. The L^2 errors and order of convergence for all these methods are summarized in Figure 4.2 and Table 4.1.

A comparison of the exact functions with some of the mixed finite element approximations can be seen in Figures 4.3 and 4.4. In all cases, the finite element solutions for the concentrations look very similar to the exact solutions. The RT^0/P_{dc}^0 solution shows small wiggles in the mole fraction isolines due to the piecewise constant approximation of this variable. On Figures 4.5 and 4.6, the fluxes computed by the RT^1/P_{dc}^1 mixed finite element method look similar to the exact fluxes. We only show



Figure 4.1: Uniform triangular mesh, 40x40 grid, 3200 elements

Table 4.1: The slopes of the least squares best fit to the $-\ln(E)$ vs. $-\ln(h)$ data for each of the finite element methods

Finite Element Method	Slope for ξ	Slope for J
Standard P^2	3.0001	2.0059
Standard P^1	1.9999	0.9999
RT^1/P_{dc}^1	1.9997	1.9997
RT^0/P_{dc}^0	0.9988	0.9988
RT^1/P^1	2.0073	1.0038
BDM^1/P_{dc}^0	1.0000	1.0038

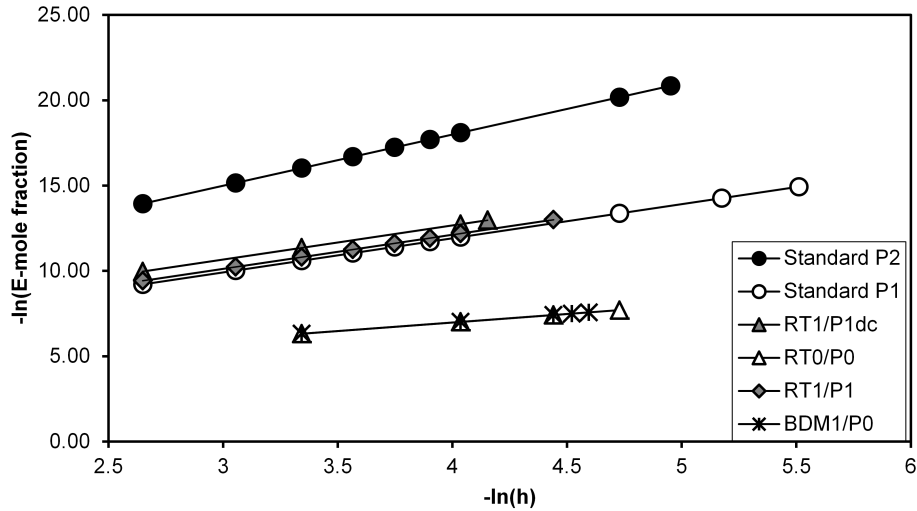
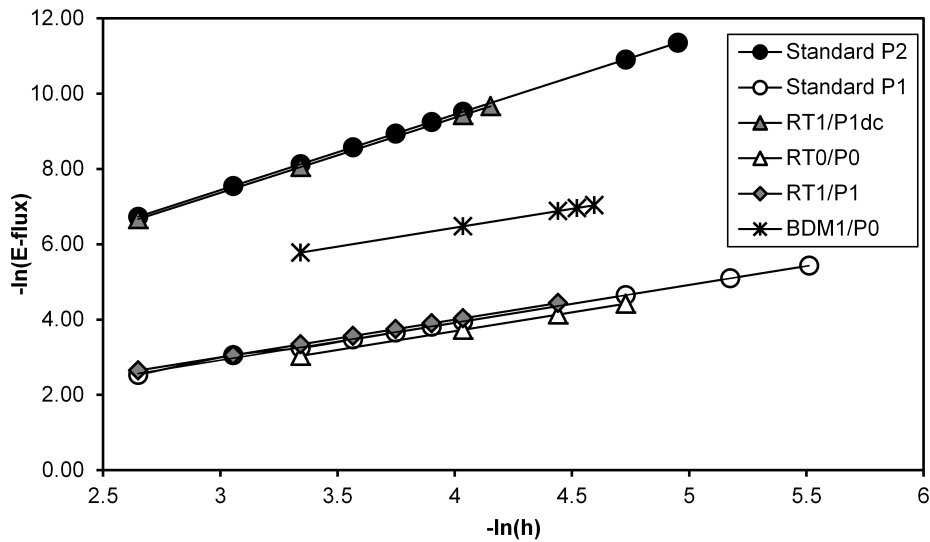
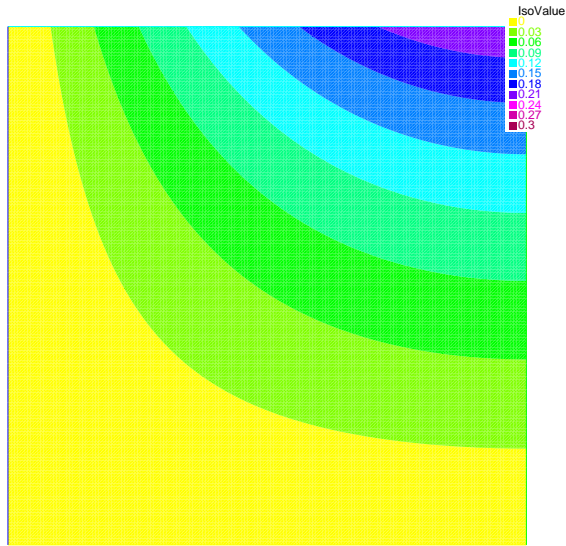
(a) Plot for $-\ln(E_\xi)$ vs. $-\ln(h)$ (b) Plot for $-\ln(E_J)$ vs. $-\ln(h)$

Figure 4.2: Plots comparing the errors of the different finite element methods with respect the number of elements in the mesh. A comparison of the mole fraction errors is given in (a) and a comparison of the molar flux errors is given in (b)

the flux calculated using the RT^1/P_{dc}^1 method since the other methods yield identical results.

For RT^0/P_{dc}^0 and BDM^1/P_{dc}^0 it can be seen that both the mole fractions and the fluxes have a first order convergence rate. Similarly RT^1/P_{dc}^1 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_{dc}^k method has. However, when we attempt to recover the flux from the standard finite element solution we lose an order of accuracy.



(a) Exact solution

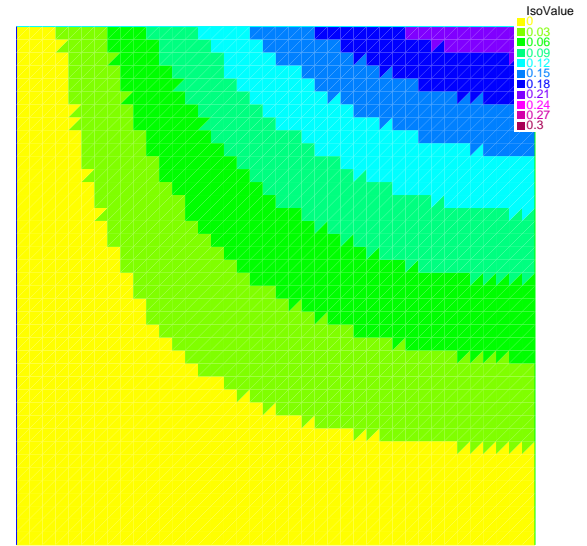
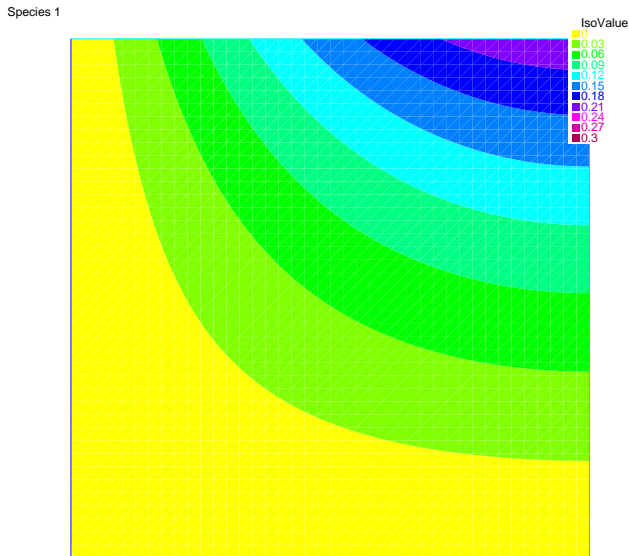
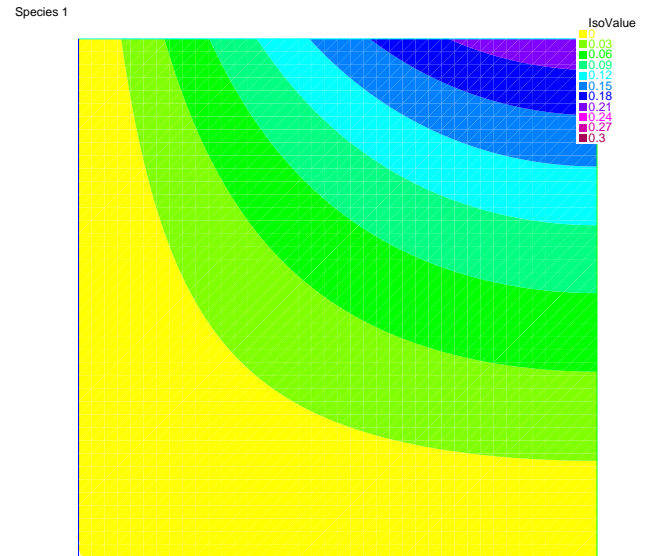
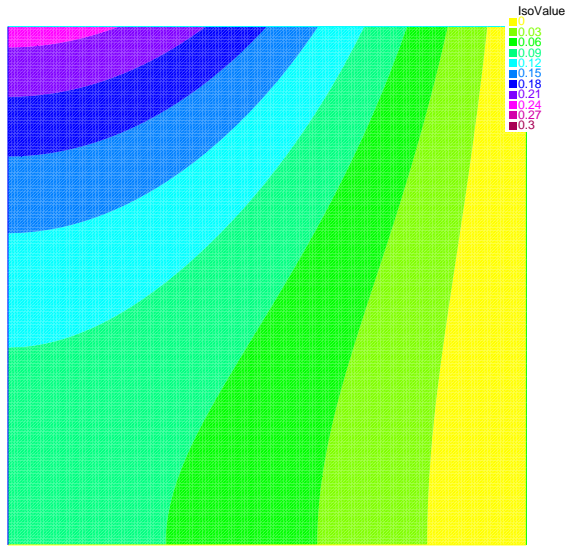
(b) RT^0/P_0 (c) RT^1/P^1 (d) RT^1/P^1_{dc}

Figure 4.3: Comparison of the exact and numerical solutions for ξ_1 . Results are shown on the mesh with 3200 elements.



(a) Exact solution

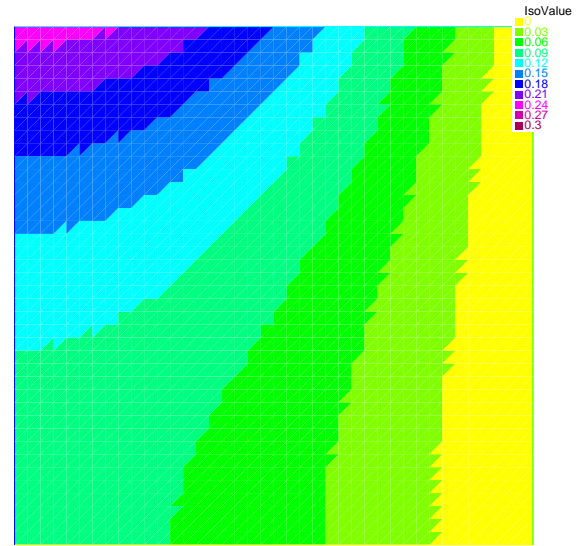
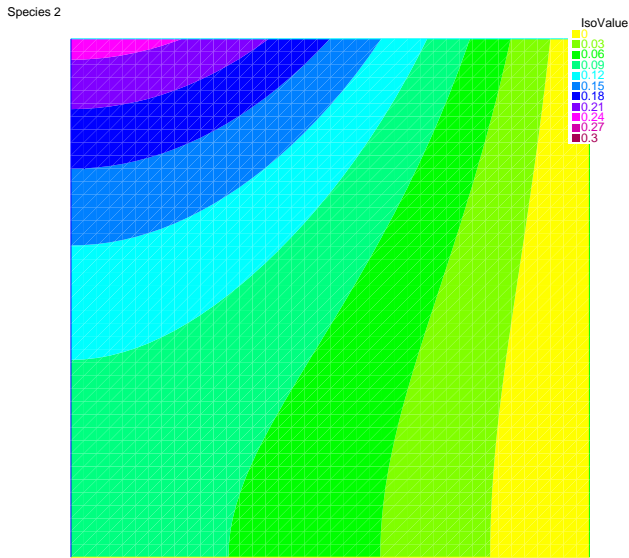
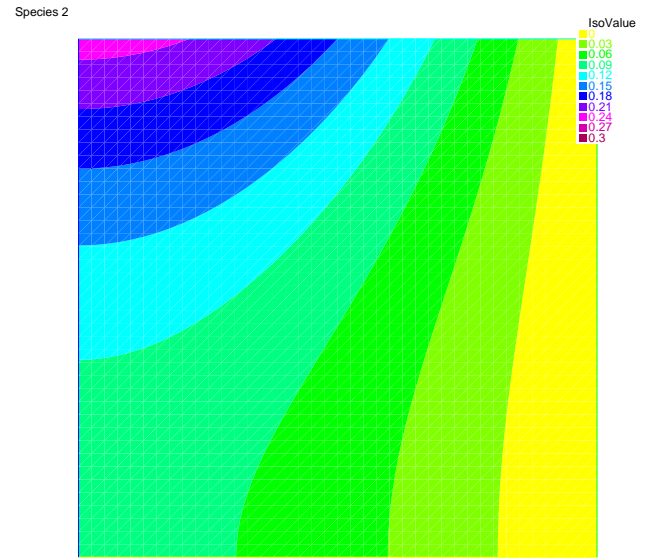
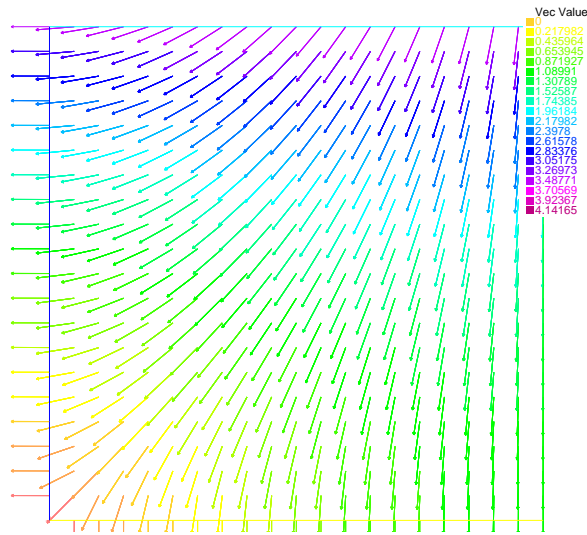
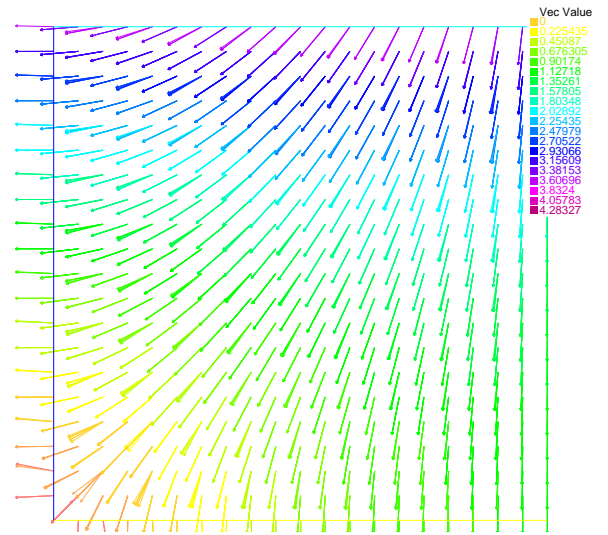
(b) RT^0/P_0 (c) RT^1/P^1 (d) RT^1/P^1_{dc}

Figure 4.4: Comparison of the exact and numerical solutions for ξ_2 . Results are shown on the mesh with 3200 elements.

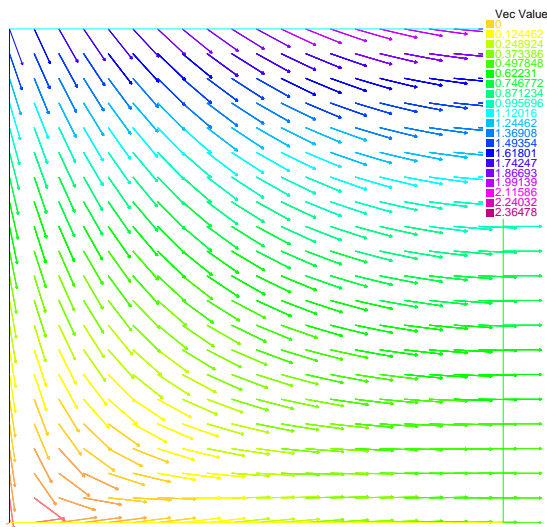


(a) Exact Solution

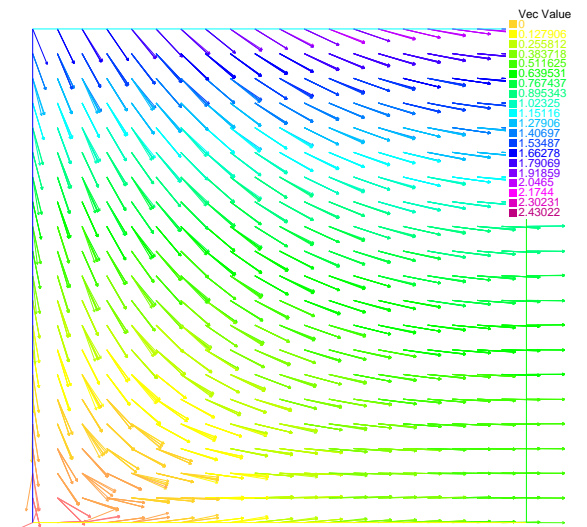


(b) $RT^1/P1_{dc}$

Figure 4.5: Plots for the flux J_1 . Here the colour of the arrow represents the magnitude of the flux.



(a) Exact solution



(b) $RT^1/P1_{dc}$

Figure 4.6: Plots for the flux J_2 . Here the colour of the arrow represents the magnitude of the flux.

4.3 Mazumder Test Case

In this test case we have a 10cm by 10cm box with three openings. One opening on the bottom, one on the top, and one to the left as seen in Figure 4.7. For this we take no flux boundary conditions away from the openings (Γ_N), and a Dirichlet condition at the openings (Γ_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 [17] where all the binary diffusion coefficients are equal and the second proposed in [4] 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 .

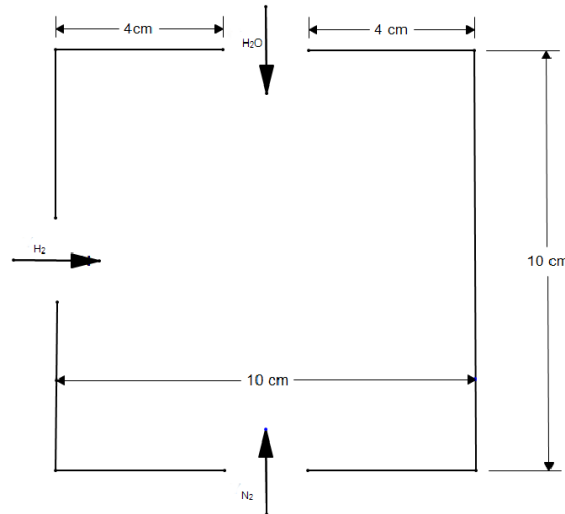


Figure 4.7: Diagram showing the geometry for test cases 2 and 3.

For these test cases, mixed finite element methods were applied to the mass formulation of the Stefan-Maxwell equations as in [4]. This way the mass fractions, Y_i , and mass fluxes, j_i , could be computed directly. The mass formulation is found using the following equalities:

$$\xi_i = \frac{MY_i}{m_i} \text{ and } J_i = \frac{j_i}{m_i}, \quad (4.3.1)$$

where m_i is the mass of species i and M is the mass of the mixture. The concentration

term c_{tot} was also replaced with ρ/M , where ρ is the density of the mixture. The mass formulation of the Stefan-Maxwell equations is:

$$-\nabla \frac{MY_i}{m_i} = \frac{M^2}{\rho} \sum_{j=1}^n \frac{Y_j j_i - Y_i j_j}{m_i m_j D_{ij}}, \quad (4.3.2)$$

$$\nabla \cdot \frac{j_i}{m_i} = r_i, \quad (4.3.3)$$

$$\sum_{i=1}^n Y_i = 1, \quad (4.3.4)$$

$$\sum_{i=1}^n j_i = 0. \quad (4.3.5)$$

We can proceed to put the mass formulation into a mixed variational formulation as we did with the mole formulation. When this is done we arrive at the following bilinear form $a(\cdot, \cdot)$ for ternary diffusion:

$$a(j, q) = \int_{\Omega} \frac{M^2}{\rho} \left(\left(\frac{1}{m_1 m_3 D_{13}} - \bar{Y}_2 \alpha \right) j_1 + \bar{Y}_1 \alpha j_2 \right) \cdot q_1 \, dx \quad (4.3.6)$$

$$+ \int_{\Omega} \frac{M^2}{\rho} \left(\bar{Y}_2 \beta j_1 + \left(\frac{1}{m_2 m_3 D_{23}} - \bar{Y}_1 \beta \right) j_2 \right) \cdot q_2 \, dx, \quad (4.3.7)$$

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:

$$\rho = Y_1 m_1 + Y_2 m_2 + Y_3 m_3, \quad (4.3.8)$$

$$M = \frac{1}{\frac{Y_1}{m_1} + \frac{Y_2}{m_2} + \frac{Y_3}{m_3}}. \quad (4.3.9)$$

The other parts of the mixed formulation are found just by substituting in 4.3.1. With this formulation we can now proceed with the next two test cases.

For the Mazumber test case all the binary diffusion coefficients are taken to be equal to $10 \text{ cm}^2/\text{s}$. The value of the coefficient will not change the solution for the mass fractions [4], it will however change the flux. A non-uniform mesh was created using FreeFEM++'s "buildmesh" function. The mesh can be seen in Figure 4.8.

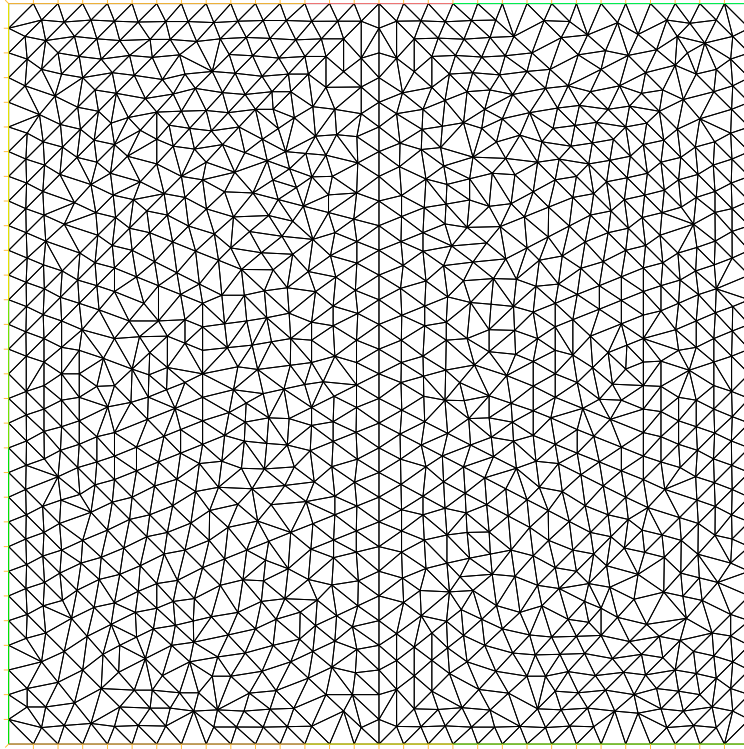


Figure 4.8: Mesh containing 2,148 triangles, used to compute solution to Mazumder test cases. Generated using FreeFEM++ buildmesh function

The computation was performed using the given mesh and the mixed finite element method RT^1/P_{dc}^1 . The simulation took 631 nonlinear iterations with a direct linear solver and $\sigma = 0.03$. The heavy under relaxation was necessary to achieve convergence of the fixed point. The calculation required a CPU time of 22 minutes. Computations were performed using the $RT0/P0$ method and were visually similar to the $RT1/P1dc$ method. The main difference was that the isolines 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 below in Figure 4.9 and 4.10. Visual they are identical to the mass fraction plots found in [4] calculated on an 80×80 grid using quadratic polynomial elements (P^2).

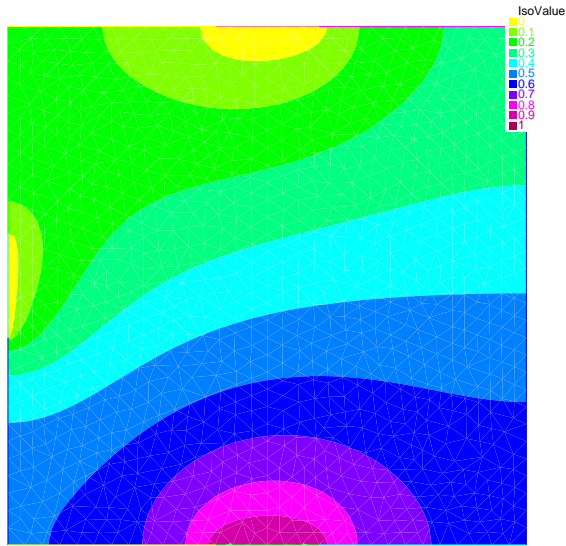
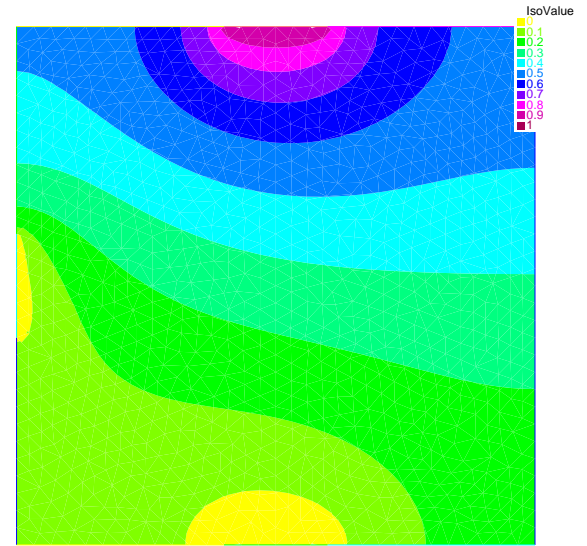
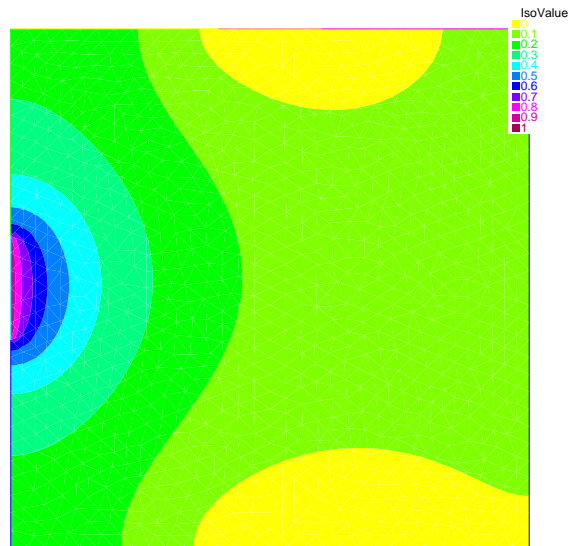
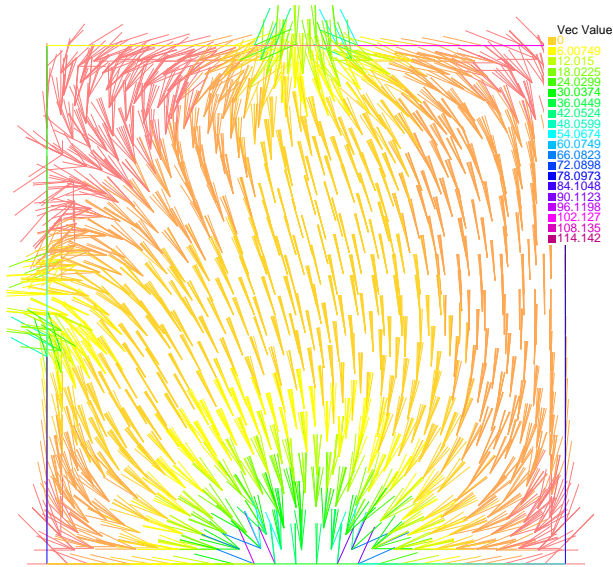
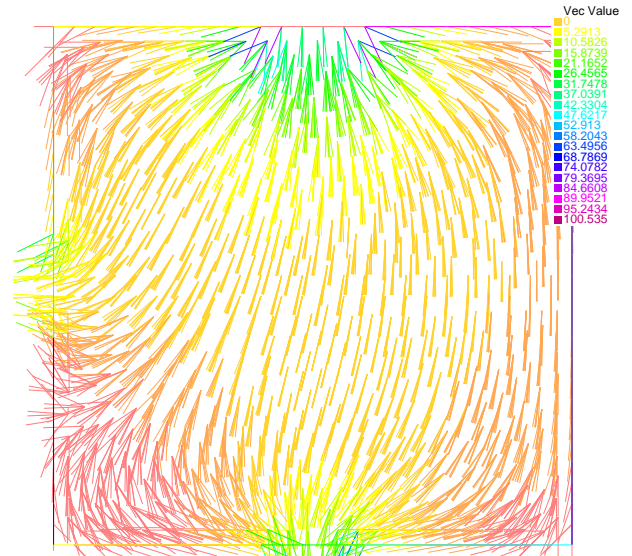
(a) Mass fraction of N_2 (b) Mass fraction of H_2O (c) Mass fraction of H_2

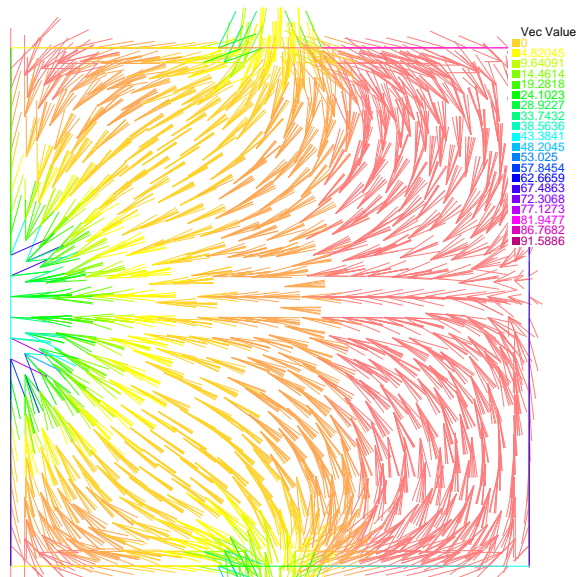
Figure 4.9: Plots of the mass fractions for the Mazumder steady state test where all binary diffusion coefficients are taken to be 1



(a) Molar flux of N_2



(b) Molar flux of H_2O



(c) Molar flux of H_2

Figure 4.10: Plots of the mass fluxes for the Mazumder steady state test where all binary diffusion coefficients are taken to be equal

The third test case was presented in [4]. 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 α and β are not zero in either test case 2 or 3 the fixed point iteration converges in the same number of iterations. The mass fraction plots from [4] were computed using P^2 elements on a mesh with 6400 grid points and are visually identical to ones in Figure 4.11. Despite the large difference in binary diffusion coefficients the mass fraction plots are quite similar when compared to the equal diffusion case. Plots for the mass fluxes are shown in Figure 4.12. 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.

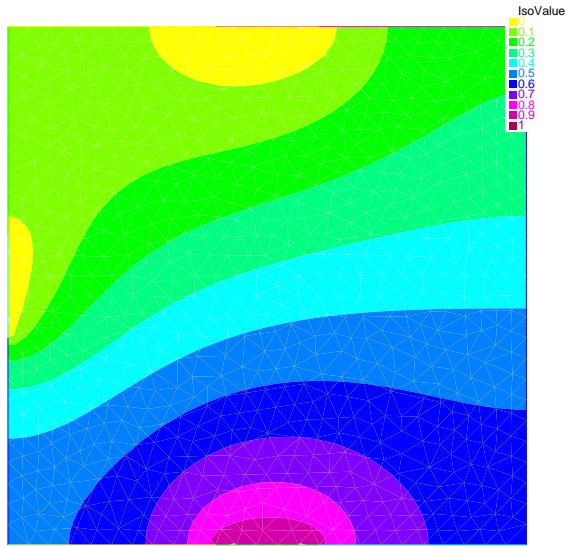
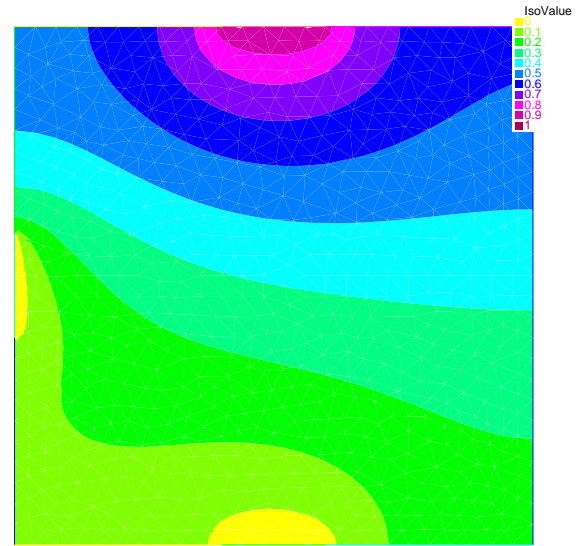
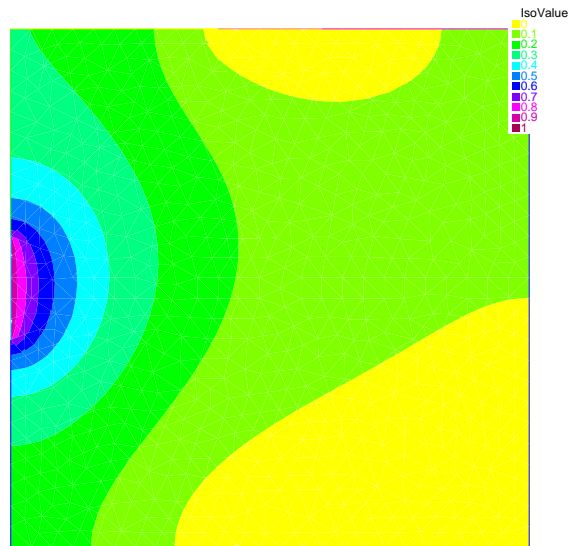
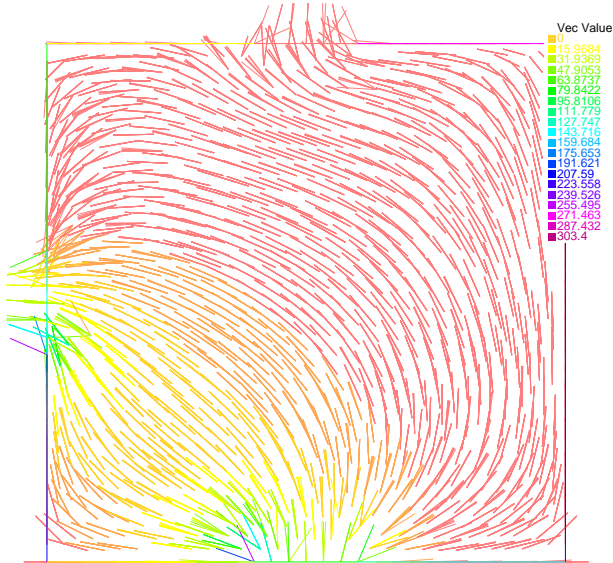
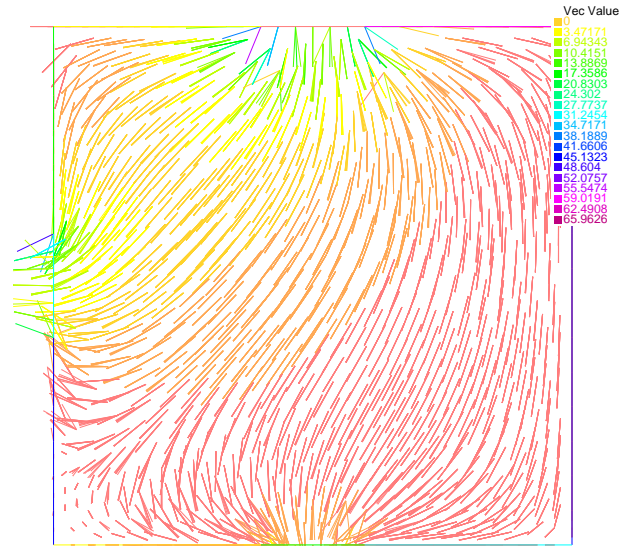
(a) Mass fraction of N_2 (b) Mass fraction of H_2O (c) Mass fraction of H_2

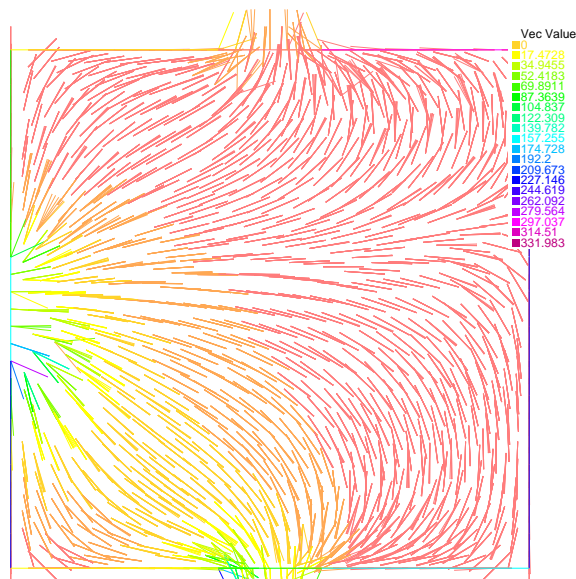
Figure 4.11: Plots of the mass fractions for the steady state test where the binary diffusion coefficients are taken as $D_{N_2-H_2O} = 1$, $D_{N_2-H_2} = 10$, and $D_{H_2-H_2O} = 100$



(a) Molar flux of N_2



(b) Molar flux of H_2O



(c) Molar flux of H_2

Figure 4.12: Plots of the molar fluxes for the steady state test where the binary diffusion coefficients are taken as $D_{N_2-H_2O} = 1$, $D_{N_2-H_2} = 10$, and $D_{H_2-H_2O} = 100$

Chapter 5

Conclusion

The contributions of the thesis are now summarized and future work is considered.

5.1 Contribution of this Thesis

In this thesis the Stefan-Maxwell equations for the diffusion of n species were considered in the context of abstract saddle point problems. Such a setting was never investigated for these equations. A main benefit is the ability to solve for both the fluxes and the molar fractions without rewriting the Stefan-Maxwell equations. The difficulty in the application of the mixed finite element theory to the Stefan-Maxwell equations is the presence of several primal and dual variables, all linked together through a degenerate system of partial differential equations. To remove this degeneracy, we had to express one variable from the others and find a strategy to have a generic substitution technique that applies to n -ary diffusion. While we could propose a variational formulation for n -ary diffusion, the analysis of the well-posedness of the problem stands only in the ternary case, and only after a linearization of the system. In the case of quaternary diffusion and above, using the Gershgorin circle theorem to obtain lower bounds on the eigenvalues of the quadratic form becomes

very cumbersome and alternate technique would be recommended.

In chapter 2, a mixed variational formulation was derived for a linearized version of the n-ary Stefan-Maxwell equations. Then the case of ternary diffusion was analyzed and shown to be well-posed when the binary diffusion coefficients were within a certain range of each other. In much of the literature the well-posedness of the Stefan-Maxwell equations is not considered. While the considerations of chapter 2 were for a linearized version of the Stefan-Maxwell equations, investigation of the fixed point could extend the work of chapter 2 to conditions for the well-posedness of the fully nonlinear Stefan-Maxwell equations.

In chapter 3, the linearized mixed variational formulation was discretized using a mixed finite element approach. Applying standard theory for mixed finite element methods showed that whenever the linearized Stefan-Maxwell equations were well-posed, then properly chosen mixed finite element methods converge. An investigation into the fixed point could also extend the theoretical results of the numerical method to the nonlinear case.

The method was tested explicitly in chapter 4 on a manufactured problem. Here the error estimates from chapter 3 were explicitly confirmed through numerical tests. It was also shown that an order of convergence is lost when calculating the flux using standard methods. Two other numerical test cases were considered and compared to other solutions attempted in the literature. A main contribution of this chapter is that it shows that the mixed finite element method can be used to get species concentration solutions similar to the literature, while also getting information about species flux. Furthermore, the mesh size needed for solution convergence was smaller than in previous work.

5.2 Future Work

Some areas for future work:

1. Expand on the conditions for when the method is well-posed. One of the tests performed in this paper went way outside the conditions for proven well-posedness. Additionally, the condition of coerciveness of the bilinear form $a(\cdot, \cdot)$ is stronger than necessary, a weaker pair of inf-sup conditions are all that is necessary for well-posedness of the saddle point problem.
2. Investigate the fixed point method used to determine conditions for when it converges and when it does not.
3. Apply the mixed finite element to more applied engineering problems e.g. in fuel cells or biology, perhaps involving time dependent phenomena.

Bibliography

- [1] N.S. Abdullah and D.B. Das. Modelling nutrient transport in hollow fibre membrane bioreactor for growing bone tissue with consideration of multi-component interactions. *Chemical Engineering Science*, 62(21):5821–5839, 2007.
- [2] K.E. Atkinson and W. Han. *Theoretical Numerical Analysis: A Functional Analysis Framework*. Mathematics and Statistics. Springer-Verlag New York, 2009.
- [3] D. Bothe. On the Maxwell-Stefan Approach to Multicomponent Diffusion. In Joachim Escher, Patrick Guidotti, Matthias Hieber, Piotr Mucha, Jan W. Prüss, Yoshihiro Shibata, Gieri Simonett, Christoph Walker, and Wojciech Zajączkowski, editors, *Parabolic Problems*, volume 80 of *Progress in Nonlinear Differential Equations and Their Applications*, pages 81–93. Springer Basel, 2011.
- [4] K. Bottcher. Numerical solution of a multi-component species transport problem combining diffusion and fluid flow as engineering benchmark. *International Journal of Heat and Mass Transfer*, 53(2):231–240, 2010.
- [5] A. Bressan. Lecture Notes on Sobolev Spaces. <http://www.math.psu.edu/bressan/PSPDF/sobolev-notes.pdf>, 2013.
- [6] F. Brezzi, J. Douglas, and L.D. Marini. Two families of mixed finite elements for second order elliptic problems. *Numerische Mathematik*, 47(2):217–235, 1985.

- [7] F. Brezzi and M. Fortin. *Mixed and hybrid finite elements methods*. Springer series in computational mathematics. Springer-Verlag, 1991.
- [8] B. Carnes and G. F. Carey. Local boundary value problems for the error in FE approximation of non-linear diffusion systems. *International Journal for Numerical Methods in Engineering*, 73(5):665–684, 2008.
- [9] Y.P. de Diego, F.E. Wubbolts, and P.J. Jansens. Modelling mass transfer in the PCA process using the Maxwell-Stefan approach. *The Journal of Supercritical Fluids*, 37(1):53–62, 2006.
- [10] V.V. Dilman. Combined method for studying and calculating the multicomponent diffusion in a mixture with an inert gas. *Theoretical Foundations of Chemical Engineering*, 42:166–170, 2008.
- [11] J.B. Duncan and H.L. Toor. An experimental study of three component gas diffusion , 8(1):38–41, 1962. *AIChE Journal*, 8(1):38–41, 1962.
- [12] J. Gopalakrishnan and W. Qiu. Partial expansion of a Lipschitz domain and some applications. *Frontiers of Mathematics in China*, 7:249–272, 2012.
- [13] F. Hecht. FreeFEM++. <http://www.freefem.org/ff++/ftp/freefem++doc.pdf>, 2013.
- [14] I. Hsing and P. Futerko. Two-dimensional simulation of water transport in polymer electrolyte fuel cells. *Chemical Engineering Science*, 55(19):4209–4218, 2000.
- [15] R. Krishna and J.A. Wesselingh. The Maxwell-Stefan approach to mass transfer. *Chemical Engineering Science*, 52(6):861–911, 1997.
- [16] B. Grec L. Boudin and F. Salvarani. A Mathematical and Numerical Analysis of the Maxwell-Stefan Diffusion Equations. *Discrete Contin. Dyn. Syst*, Ser. B 17(5)(3):1427–1440, 2012.

- [17] S. Mazumder. Critical assessment of the stability and convergence of the equations of multi-component diffusion. *Journal of Computational Physics*, 212(1):383–392, 2006.
- [18] K.S.C. Peerenboom, J. van Dijk, J.H.M. ten Thije Boonkkamp, L. Liu, W.J. Goedheer, and J.J.A.M. van der Mullen. Mass conservative finite volume discretization of the continuity equations in multi-component mixtures. *Journal of Computational Physics*, 230(9):3525–3537, 2011.
- [19] G. Psfogiannakis, Y. Bourgault, B.E. Conway, and M. Ternan. Mathematical model for a direct propane phosphoric acid fuel cell. *Journal of Applied Electrochemistry*, 36(1):115–130, 2006.
- [20] A. Quarteroni and A. Valli. *Numerical Approximation of Partial Differential Equations*. Springer Series in Computational Mathematics. Springer, 2008.
- [21] P.A. Raviart and J.M. Thomas. A mixed finite element method for 2-nd order elliptic problems. In Ilio Galligani and Enrico Magenes, editors, *Mathematical Aspects of Finite Element Methods*, volume 606 of *Lecture Notes in Mathematics*, pages 292–315. Springer Berlin Heidelberg, 1977.
- [22] R. Taylor and R. Krishna. *Multicomponent Mass Transfer*. Wiley Series in Chemical Engineering. Wiley, 1993.
- [23] R. Temam. Navier-Stokes Equations: Theory and Numerical Analysis. In *Navier-Stokes Equations: Theory and Numerical Analysis*, volume 2 of *Studies in Mathematics and Its Applications*, pages iv–. Elsevier, 1976.