Electrochemical Behavior of Bipolar Membranes

By

Nathan Patrick Craig

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor John Newman, Chair
Professor David Graves
Professor Tarek Zohdi

Fall 2013
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Abstract

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The rate of recombination of ions in a weak-electrolyte solution is often controlled by the rate at which the ions collide with one another. The rate of collision has been previously treated in the literature, resulting in a classic expression for the rate constant. A derivation is presented here employing the methodology of Onsager and Fuoss. This methodology makes use of a distribution function to track the relative average positions of the two reactants. The reactants are assumed to undergo movement that follows a Nernst-Planck Equation for the migration and diffusion components of the flux. The potential of interaction of the ions is assumed to be a coulomb potential screened by an ion cloud formed by a supporting electrolyte. The resulting expression for the rate constant is the same as that of Debye.

The dissociation of weak electrolytes is increased by an applied electric field. Lars Onsager's classic treatment of this increase in dissociation determines the effect of an applied electric field upon the movement of a pair of ions formed by dissociation. To obtain an analytic expression, Onsager approximates that the pair of ions form a chemical bond when they are at a separation distance of zero. This approximation is poor when long chemical bonds are involved, such as the dissociation of an electrolyte occurring via charge transport along a hydrogen-bond wire.

Here, the work of Onsager is extended to the case of dissociation via long chemical bonds. For bond lengths greater than zero, the results predict the recombination rate constant of a collision-controlled reaction will increase with an applied electric field. Additionally, results predict that the dissociation of a weak electrolyte will increase with an applied electric field. The increase in dissociation is predicted to vary by orders of magnitude with small changes in the length of the chemical bond.

A 1-d continuum model of a bipolar membrane is shown. The model accounts for the diffusion and migration of species, electrostatics, and chemical reaction. The bipolar membrane model is seen to rectify current and undergo breakdown. This is the first model to use a model of water splitting at large electric fields to predict the breakdown of the junction. A layer of weak base is included in the junction of the membrane as a catalyst layer. Model results show agreement with published experimental results. The effect of the catalyst layer is seen to be negligible. The ineffectiveness of the catalyst is attributed to the greater increase in water.
dissociation due to the electric field than by the catalyst mechanism. Results are shown for a bipolar membrane immersed in a neutral pH solution as well as a bipolar membrane separating a solution with a pH of 2 from a solution with a pH of 12.
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Acknowledgements

I am very thankful to each person who has helped me complete this dissertation. I would like to start by thanking Professor Newman. His intellectual curiosity and scientific rigor have challenged me to be a better engineer. I have benefited greatly from his knowledge of electrochemical systems. I am grateful that I have had the opportunity to work with him on this research. I am proud to be a student of his.

I would like to thank the fellow members of the Newman lab who have contributed to my understanding of this material. The group members include Charles Delacourt, Paul Albertus, Lisa Onishi, Penny Gunterman, Ryan Balliet, and Maureen Tang. I would especially like to thank Anthony Ferrese and Alan Berger for being here with me at the end.

I would like to thank my roommates throughout graduate school. My roommates Craig Dana, David Wong and Anthony Ferrese have helped shape me as a person and have supported me through many of the trials of graduate school.

I would like to thank all of the authors who have influenced this research. I have spent much of my time in graduate school studying a number of textbooks and papers, many of which are not found in the references for this dissertation as the work is on separate topics. However, I have benefited greatly from these authors.

I would like my family. I thank my parents, Steve and Jean, for their support and love throughout all of graduate school. Always knowing that my parents were pulling for me and praying for me has been immensely encouraging. I also thank my siblings, Nicole, Natalie and Nick for believing in me every step of the way.

Lastly, I would like to thank the newest member of my family, my wife Joanne. Joanne has added a new spark to my life. She has challenged me intellectually on many diverse topics. She has helped me finish this dissertation through support and encouragement. But most importantly, she has been a source of love in my life. I am excited for what the future holds for the two of us.
Chapter 1: Collision-Controlled Reactions in Solution

Abstract

The rate of recombination of ions in a weak-electrolyte solution is often controlled by the rate at which the ions collide with one another. The rate of collision has been previously treated in the literature, resulting in a classic expression for the rate constant. A derivation is presented here employing the methodology of Onsager and Fuoss.\(^1\) This methodology makes use of a distribution function to track the relative average positions of the two reactants. The reactants are assumed to undergo movement that follows a Nernst-Planck Equation for the migration and diffusion components of the flux. The potential of interaction of the ions is assumed to be a coulomb potential screened by an ion cloud formed by a supporting electrolyte. The resulting expression for the rate constant is the same as that of Debye.\(^2\)

Introduction

The rate at which ions will collide in solution has received extensive treatment. The first treatment of a similar subject is due to Langevin.\(^3\) Langevin derived an expression for the rate at which ions recombine in an ionized gas. His treatment assumes ions of zero size that move by migration alone due to the influence of coulomb potentials acting between ions. The resulting expression is valid for a system satisfying two conditions. The first condition is that the ions should recombine when approaching distances less than the Bjerrum length. The second condition is that the system of interest must be composed of a dilute concentration of ions in a dense gas. This assures that the motion can be described using a diffusion coefficient and that the potential of interaction is well approximated by an unshielded coulomb potential.

Chronologically, the next treatment of a similar subject is due to Smoluchowski.\(^4\) Smoluchowski treated the rate of aggregation of colloidal particles. The method used assumed uncharged colloidal particles that move due to diffusion. The resulting expression includes a characteristic length which was taken to be the sum of the radii of the two particles. This is the distance at which the particles collide.

Onsager later treated a similar problem while focusing on the dissociation of weak electrolytes in the presence of high fields.\(^5\) Using the distribution function of Onsager and Fuoss,\(^1\) the derivation yields the same expression as Langevin.

Finally, Debye treated the problem, extending it to include the effect of an ion cloud shielding the recombining ions.\(^2\) Debye's expression is the most general of the expressions of interest. In the limiting case of an infinite Debye length and a recombination distance of zero, Debye's expression reduces to Langevin's expression. In the limiting case of infinite Debye length and uncharged particles, Debye's expression reduces to the expression of Smoluchowski. Debye indicates that he believes that his treatment applies to situations in which the recombining ions are at some finite yet small concentration. This is not strictly true. Debye's expression assumes an equilibrium ion cloud around each of the reacting particles. Such a situation occurs in the event of equilibrium between the recombination and dissociation reactions, or in the event of a supporting electrolyte. In the situation in which the recombination reaction rate is much larger than the dissociation rate, the reacting ions will have a surrounding ion cloud. However, the ion cloud will not be at equilibrium due to the ions undergoing a net reaction.
In the treatment presented here, the distribution function of Onsager and Fuoss will be used to derive the same expression as that of Debye for the recombination rate constant of a collision-controlled reaction. The derivation of the governing equation for the distribution function follows that of Onsager, modified to include the effect of an ion cloud. The potential due to the ion cloud is derived following Newman. The resulting continuity equation for the distribution function is the same as the governing equation solved by Debye. In the treatment presented here, the governing equation is solved using a singular-perturbation method. This is different from the solution method used by Debye, but achieves the same result.

Overall, this chapter is largely an amalgamation of work present in the literature. It was deemed worthwhile to include this chapter for two reasons. The first reason is that Chapter 2 of this thesis calculates the influence of an applied electric field upon the dissociation of water. The calculation in Chapter 2 builds upon the work of Onsager for the increase in dissociation due to the applied electric field. An understanding of the current chapter is essential for an understanding of the derivation in Chapter 2. The second reason for including this chapter is that some authors seem to be confused about the expression for the rate constant. For example, the current derivation results in an expression in which \( k_{-1} \propto D_i + D_j \). Some authors incorrectly believe that this is due to an assumption. The derivation presented here results in \( k_{-1} \propto D_i + D_j \) without any additional assumptions. The result \( k_{-1} \propto D_i + D_j \) is physically plausible since any expression for the rate constant must be symmetric in the diffusivities of the two ions.

**Material Balance**

In the system of interest, a homogeneous chemical reaction is occurring. The reaction can be represented as

\[
i + j \rightleftharpoons m,
\]

where \( i, j, \) and \( m \) represent species present in a solution. Three macroscopic material balances for the various species can be written as

\[
\frac{\partial n_m}{\partial t} = -\nabla \cdot N_m - k_1 n_m + k_{-1} n_i n_j,
\]

\[
\frac{\partial n_i}{\partial t} = -\nabla \cdot N_i + k_1 n_m - k_{-1} n_i n_j,
\]

and

\[
\frac{\partial n_j}{\partial t} = -\nabla \cdot N_j + k_1 n_m - k_{-1} n_i n_j.
\]

In these macroscopic material balances, \( n_x \) is the number of \( x \) particles per volume, \( \underline{N}_x \) is the flux of \( x \) particles, \( k_1 \) is the rate constant for the dissociation reaction, and \( k_{-1} \) is the rate constant for the recombination reaction. This chapter details the derivation of an expression for \( k_{-1} \) in the case where the reaction is controlled by how often the reacting particles collide.

**Distribution Functions**

In order to treat the statistical physics of particle collisions, Onsager and Fuoss's distribution function is used. Imagine a solution containing particles of type \( i \) and particles of type \( j \). In this solution, imagine that there are two small control volumes \( dV_1 \) and \( dV_2 \) located at
positions \( r_1 \) and \( r_2 \), respectively. These control volumes are so small that they can contain only a single particle at a time. The geometry of these control volumes is given in Figure 1.1.

![Control Volumes](image)

**Figure 1.1.** The geometry of the control volumes used in defining the distribution function.

Onsager and Fuoss imagine four different clocks. A clock with time denoted by \( t_j \) runs when a particle of type \( j \) is in \( dV_1 \). A clock with time denoted by \( t_i \) runs when a particle of type \( i \) is in \( dV_2 \). A clock with time denoted by \( t_{ji} \) runs when an ion of type \( j \) is in \( dV_1 \) and a particle of type \( i \) is in \( dV_2 \). Lastly, a clock with time denoted by \( t \) keeps track of the total amount of time passed.

Using the clocks, the fraction of the total time that a particle of type \( j \) is in \( dV_1 \) is given by the expression

\[
\frac{t_j}{t} = n_j dV_1. \tag{1.5}
\]

Similarly, the fraction of the total time that a particle of type \( i \) is in \( dV_2 \) is given by the expression

\[
\frac{t_i}{t} = n_i dV_2. \tag{1.6}
\]

To write the fraction of the total time that a particle of type \( j \) is in \( dV_1 \) and a particle of type \( i \) is in \( dV_2 \), additional concentrations are defined. The concentration \( n_{ij} \) denotes the concentration of ions of type \( i \) in the vicinity of a particle of type \( j \). The concentration \( n_{ij} \) denotes the concentration of ions of type \( j \) in the vicinity of a particle of type \( i \). These concentrations are functions of both \( r_1 \) and \( r_2 \). The additional concentrations, \( n_{ji} \) and \( n_{ij} \), are introduced because it is expected that the concentration of particles is affected when the particles are charged ions. The concentration of the ions affected by the presence of other ions due to forces exerted between pairs of ions. The vicinity in which these forces act is characterized by the Debye length. Of the time that a particle of type \( j \) is in \( dV_1 \), the fraction that a particle of type \( i \) is in \( dV_2 \) is given by the expression

\[
\frac{t_{ji}}{t_j} = n_{ji} dV_2. \tag{1.7}
\]

Additionally, of the time that a particle of type \( i \) is in \( dV_2 \), the fraction that a particle of type \( j \) is in \( dV_1 \) is given by the expression...
\[
\frac{t_{ji}}{t_i} = n_{ij} \text{d}V_1.
\]

(1.8)

By combining Equations 1.5, 1.6, 1.7, and 1.8, the expression for the chance of finding simultaneously a ion of type j in dV_1, and a particle i in dV_2 is given by

\[
\frac{t_{ji}}{t_i} = n_j n_{ii} \text{d}V_1 \text{d}V_2 = n_i n_{ij} \text{d}V_1 \text{d}V_2.
\]

(1.9)

Using Equation 1.9, the distribution function is defined as

\[
f_{ji} = f_{ij} = n_j n_{ii} = n_i n_{ij}.
\]

(1.10)

In Equation 1.10, \(f_{ij}\) is the distribution function. The distribution function is a function of both \(r_1\) and \(r_2\).

Additionally, the average velocity of a particle of type i in the vicinity of a particle of type j will be denoted as \(v_{ji}\). The average velocity of a particle of type j in the vicinity of a particle of type i will be denoted as \(v_{ij}\). Both of these velocities are functions of \(r_1\) and \(r_2\).

To derive the continuity equation for the distribution function, the problem is considered in a 6-dimensional space. Three coordinates are associated with \(\text{d}V_1\) : \(\xi_1, \xi_2,\) and \(\xi_3\). Similarly, three coordinates are associated with \(\text{d}V_2\) : \(\xi_4, \xi_5,\) and \(\xi_6\). Consider the 6-dimensional cube located at \(\xi_1, \xi_2, \xi_3, \xi_4, \xi_5,\) and \(\xi_6\) with side lengths \(\Delta\xi_1, \Delta\xi_2, \Delta\xi_3, \Delta\xi_4, \Delta\xi_5,\) and \(\Delta\xi_6\). The distribution function in the cube is \(f_{ji}\). The components of the average velocity of the ion of type j in \(\text{d}V_1\) are \(v_{j1}, v_{j2}, v_{j3}\). The components of the average velocity of the ion of type i in \(\text{d}V_2\) are \(v_{i4}, v_{i5}, v_{i6}\). The continuity equation for the distribution function is then

\[
\frac{\partial f_{ji}}{\partial t} \Delta\xi_1 \Delta\xi_2 \Delta\xi_3 \Delta\xi_4 \Delta\xi_5 \Delta\xi_6 = - \sum_{m=1}^{6} \frac{\partial (\xi_m f_{ji})}{\partial \xi_m} \Delta\xi_m \Delta S_m.
\]

(1.11)

In Equation 1.11, \(\xi_m\) is the m\(^{th}\) coordinate, \(\Delta\xi_1 \Delta\xi_2 \Delta\xi_3 \Delta\xi_4 \Delta\xi_5 \Delta\xi_6\) is the volume of the infinitesimal six dimensional cube, \(\dot{\xi}_m\) is the time derivative in the m\(^{th}\) coordinate and \(\Delta S_m\) is the surface area of the face normal to the m\(^{th}\) coordinate so that \(\Delta S_1 = \Delta\xi_2 \Delta\xi_3 \Delta\xi_4 \Delta\xi_5 \Delta\xi_6\). To simplify the notation, divergence operators \(\nabla_1 \cdot\) and \(\nabla_2 \cdot\) are introduced, such that

\[
\nabla_1 \cdot + \nabla_2 \cdot = \sum_{m=1}^{6} \frac{\partial}{\partial \xi_m}.
\]

(1.12)

Since the time derivative of the m\(^{th}\) coordinate is given by \(\dot{\xi}_m\), then \(v_{ji} = (\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3)\) and \(v_{ij} = (\dot{\xi}_4, \dot{\xi}_5, \dot{\xi}_6)\). Dividing by the volume element allows us to rewrite the continuity equation, Equation 1.11, as

\[
\frac{\partial f_{ji}}{\partial t} = - \nabla_1 \cdot (v_{ji} f_{ji}) - \nabla_2 \cdot (v_{ij} f_{ji}).
\]

(1.13)

Equation 1.13 is the general continuity equation for the distribution function derived by Onsager and Fuoss. In Equation 1.13, \(f_{ji}, v_{ji},\) and \(v_{ij}\) are each functions of \(r_1\) and \(r_2\).

The system of interest in this chapter is macroscopically uniform. Because of this, the absolute positions of \(\text{d}V_1\) and \(\text{d}V_2\) do not matter, only the relative position of \(\text{d}V_1\) to \(\text{d}V_2\) matters. The continuity equation can then be rewritten using the coordinate \(r = r_2 - r_1\). By denoting the coordinates of \(r\) as \(\xi_7, \xi_8,\) and \(\xi_9\), a coordinate transformation of the divergence operators leads to
\[ \nabla_1 = \frac{\partial \xi_7}{\partial \xi_1} \frac{\partial}{\partial \xi_7} + \frac{\partial \xi_8}{\partial \xi_2} \frac{\partial}{\partial \xi_8} + \frac{\partial \xi_9}{\partial \xi_3} \frac{\partial}{\partial \xi_9} = -\nabla, \tag{1.14} \]

and

\[ \nabla_2 = \frac{\partial \xi_7}{\partial \xi_4} \frac{\partial}{\partial \xi_7} + \frac{\partial \xi_8}{\partial \xi_5} \frac{\partial}{\partial \xi_8} + \frac{\partial \xi_9}{\partial \xi_6} \frac{\partial}{\partial \xi_9} = \nabla. \tag{1.15} \]

Using Equations 1.14 and 1.15, the continuity equation can be written as

\[ \frac{\partial f_{ji}}{\partial t} = \nabla \cdot \left( f_{ji} (\nabla_j - \nabla_i) \right). \tag{1.16} \]

Equation 1.16 is the continuity equation for the distribution function that will be solved to determine the rate of collision of reacting ions in solution. In Equation 1.16, \( f_{ji} \), \( \nabla_j \), and \( \nabla_i \) are all functions of \( r \).

Nernst-Planck Equation

It is assumed that the average velocities of the reacting ions follow a Nernst-Planck Equation. The general Nernst-Planck Equations for the movement of the ions are

\[ v_{ji} = -u_i \nabla_j U_{ji} - D_i \nabla_j \ln f_{ji} \tag{1.17} \]

and

\[ v_{ij} = -u_j \nabla_i U_{ij} - D_j \nabla_i \ln f_{ij}. \tag{1.18} \]

In Equation 1.17 and 1.18, \( u_x \) is the mobility of ions of type \( x \), and \( U_{yx} \) is the potential energy of a particle of type \( x \) in the vicinity of a particle of type \( y \).

These Equations can be rewritten using the Nernst-Einstein relation. The Nernst-Einstein relation is that \( D_x = k_B T u_x \). The Nernst-Einstein relation exists because the Nernst-Planck Equations must yield a Boltzmann distribution at equilibrium.\(^8\) Equation 1.17 and 1.18 can then be rewritten as

\[ v_{ji} = -\frac{D_i}{k_B T} \left( \nabla_j U_{ji} + k_B T \nabla_j \ln f_{ji} \right) \tag{1.19} \]

and

\[ v_{ij} = -\frac{D_j}{k_B T} \left( \nabla_i U_{ij} + k_B T \nabla_i \ln f_{ij} \right). \tag{1.20} \]

In these expressions, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The continuity equation, Equation 1.16, contains the difference in the velocities. This velocity difference is given by

\[ v_{ij} - v_{ji} = \frac{D_i}{k_B T} \left( \nabla_j U_{ji} + k_B T \nabla_j \ln f_{ji} \right) - \frac{D_j}{k_B T} \left( \nabla_i U_{ij} + k_B T \nabla_i \ln f_{ij} \right). \tag{1.21} \]

The velocity difference can also be rewritten using the coordinate \( r \). The coordinate transformation of the gradient operators leads to

\[ \nabla_1 = \hat{e}_1 \frac{\partial \xi_7}{\partial \xi_1} \frac{\partial}{\partial \xi_7} + \hat{e}_2 \frac{\partial \xi_8}{\partial \xi_2} \frac{\partial}{\partial \xi_8} + \hat{e}_3 \frac{\partial \xi_9}{\partial \xi_3} \frac{\partial}{\partial \xi_9} = -\nabla, \tag{1.22} \]

and

\[ \nabla_2 = \hat{e}_1 \frac{\partial \xi_7}{\partial \xi_4} \frac{\partial}{\partial \xi_7} + \hat{e}_2 \frac{\partial \xi_8}{\partial \xi_5} \frac{\partial}{\partial \xi_8} + \hat{e}_3 \frac{\partial \xi_9}{\partial \xi_6} \frac{\partial}{\partial \xi_9} = \nabla. \tag{1.23} \]

Using Equations 1.22 and 1.23, the velocity difference of Equation 1.21 is transformed to
\[ v_{ji} - v_{ij} = - \frac{D_i}{k_B T} \nabla U_{ji} - \frac{D_j}{k_B T} \nabla U_{ij} - (D_i + D_j) \nabla \ln f_{ji}. \] (1.24)

This is the velocity difference that will be used in the continuity equation.

Potential Energy at Rest without External Forces

The potential energy of the ions is now calculated. To be more general, it is imagined that there is a supporting electrolyte in the system that is a strong electrolyte with ions different from the reacting ions. The ions that can undergo a reaction are of type \( i \) and type \( j \), while the ions of the supporting electrolyte are of type \( g \) and type \( h \). When the supporting electrolyte is present, it arranges itself in an ion cloud around the reacting ions. This will influence the electrostatic attraction of the two reacting ions.

It is assumed that the formation of the ion clouds occurs quickly compared to the time required for the reacting ions to collide. This is because the ion clouds are treated as being at equilibrium around the reacting ions. This is a good approximation when the concentration of the supporting electrolyte is large compared to the concentration of the reacting electrolyte.

For the system at rest, without external forces, the ions in the ion clouds follow a Boltzmann distribution. The distribution functions are then

\[
\begin{align*}
f_{\text{gi}}^0 &= f_{\text{gi}}^0 = n_i n_{\text{gi}}^0 = n_i n_{\text{gi}}^0 \exp\left(-\frac{U_{\text{gi}}}{k_B T}\right) = n_i n_{\text{gi}}^0 \exp\left(-\frac{U_{\text{gi}}}{k_B T}\right), \\
f_{\text{hi}}^0 &= f_{\text{hi}}^0 = n_h n_{\text{hi}}^0 = n_h n_{\text{hi}}^0 \exp\left(-\frac{U_{\text{hi}}}{k_B T}\right) = n_h n_{\text{hi}}^0 \exp\left(-\frac{U_{\text{hi}}}{k_B T}\right), \\
f_{\text{ig}}^0 &= f_{\text{ig}}^0 = n_i n_{\text{ig}}^0 = n_i n_{\text{ig}}^0 \exp\left(-\frac{U_{\text{ig}}}{k_B T}\right) = n_i n_{\text{ig}}^0 \exp\left(-\frac{U_{\text{ig}}}{k_B T}\right), \\
\text{and} \quad f_{\text{ih}}^0 &= f_{\text{hi}}^0 = n_i n_{\text{ih}}^0 = n_i n_{\text{ih}}^0 \exp\left(-\frac{U_{\text{ih}}}{k_B T}\right) = n_i n_{\text{ih}}^0 \exp\left(-\frac{U_{\text{hi}}}{k_B T}\right).
\end{align*}
\] (1.25)

In Equations 1.25 through 1.28, the 0 is used to indicate that the system is at rest. From Equations 1.25 through 1.28, it follows that

\[
\begin{align*}
U_{\text{gi}} &= U_{\text{ig}}, \\
U_{\text{hi}} &= U_{\text{ih}}, \\
U_{\text{gi}} &= U_{\text{ig}}, \\
U_{\text{hi}} &= U_{\text{ih}}.
\end{align*}
\] (1.29)

The electrostatic potential is governed by Poisson's Equation. Taking \( \Phi_j^0 \) to be the electrostatic potential in the vicinity of an ion of type \( j \), \( \Phi_j^0 \) is governed by

\[ \nabla^2 \Phi_j^0 = -\frac{e}{\varepsilon} (z_g n_{\text{gi}}^0 + z_h n_{\text{hi}}^0). \] (1.33)

In Equation 1.33, \( e \) is the elementary charge, \( \varepsilon \) is the dielectric permittivity, and \( z_g \) is the net number of fundamental charges on the ion of interest. Similarly, if \( \Phi_i^0 \) is the electrostatic potential in the vicinity of an ion of type \( i \), \( \Phi_i^0 \) is governed by

\[ \nabla^2 \Phi_i^0 = -\frac{e}{\varepsilon} (z_g n_{\text{gi}}^0 + z_h n_{\text{ih}}^0). \] (1.34)
In the system of interest, the concentration of reacting ions is small compared with that of the supporting electrolyte. Therefore, the concentrations present in Equations 1.33 and 1.34 are only those of the supporting electrolyte.

Combining the Boltzmann distributions with Poisson's Equation yields a Poisson-Boltzmann Equation. The two of interest are

\[ \nabla^2 \Phi_j^0 = -\frac{e}{\varepsilon} \left( z_g n_g \exp \left( -\frac{U_{jg}}{k_B T} \right) + z_h n_h \exp \left( -\frac{U_{jh}}{k_B T} \right) \right) \]  

(1.35)

and

\[ \nabla^2 \Phi_i^0 = -\frac{e}{\varepsilon} \left( z_g n_g \exp \left( -\frac{U_{ig}}{k_B T} \right) + z_h n_h \exp \left( -\frac{U_{ih}}{k_B T} \right) \right) \]  

(1.36)

At this point, expressions for the potential energies are needed. The assumption used by Debye and Hückel is that the potential energy of placing an ion of type \( g \) near an ion of type \( i \) is equal to the potential energy of placing the charge due to the ion of type \( g \) at the electrostatic potential in the vicinity of the ion of type \( i \). Making this assumption for each ion pair yields potential energies of

\[ U_{jg} = U_{gj} = z_g e \Phi_j^0 = z_j e \Phi_g^0 \]  

(1.37)

\[ U_{jh} = U_{hj} = z_h e \Phi_j^0 = z_j e \Phi_h^0 \]  

(1.38)

\[ U_{ig} = U_{gi} = z_g e \Phi_i^0 = z_i e \Phi_g^0 \]  

(1.39)

and

\[ U_{ih} = U_{hi} = z_h e \Phi_i^0 = z_i e \Phi_h^0 . \]  

(1.40)

However, as pointed out by Onsager, this assumption leads to an inconsistency. The inconsistency can be seen by realizing that Equations 1.37 through 1.40 imply that the potential is given by the number of charges on an ion multiplied by a function of the position. For example,

\[ \Phi_j^0 = z_j e G(r) , \]  

(1.41)

where \( G(r) \) is a not a function of \( z_j \). Combining Equation 1.41 with Equation 1.35 yields

\[ \nabla^2 \left( z_j e G(r) \right) = -\frac{e}{\varepsilon} \left( z_g n_g \exp \left( -\frac{z_g e^2 G(r)}{k_B T} \right) \right) + z_h n_h \exp \left( -\frac{z_h e^2 G(r)}{k_B T} \right) . \]  

(1.42)

The left side of Equation 1.42 is linear in \( z_j \) while the right side of Equation 1.42 is not. Thus, the assumption has lead to an inconsistent equation.

The inconsistency is due to an improper treatment of the statistical mechanics of the ions in the ion clouds. For example, by writing Equation 1.37 one is assuming that as an ion of type \( g \) is moved in the vicinity of an ion of type \( j \) that the resulting ion cloud is a sum of the ion clouds that are around the individual ions when they were infinitely far apart. This is not correct because the two ion clouds show an exponential dependence upon the charge of the central ion, not a linear one.

The problem can be resolved by using a "potential of mean force" as introduced by Onsager. Unfortunately, an analytic expression for the potential of mean force has not been determined in the literature. In this work, assumptions 1.37 through 1.40 will be used. This confines the applicability of the results to solutions of low concentrations.
The Poisson-Boltzmann Equation is now solved using a singular-perturbation method. The solution yields the electrostatic potential experienced by the ions and allows for the calculation of the contribution to the reaction rate due to the migration of the ions. Bjerrum arrived at an approximate solution to the Poisson-Boltzmann Equation by dividing the problem into two regions. In the outer region, he assumed the Debye-Hückel solution. In the inner region, he used the coulomb potential around a free charge. This estimation procedure is essentially a rudimentary singular-perturbation solution.

The problem is approached as a singular-perturbation problem following Newman. The problem is a singular-perturbation problem because one approximation is valid at large distances while a different approximation is valid for small distances. Neither approximation is uniformly valid. At large distances, the absolute value of the potential energy is taken to be small. At small distances, the number of ions present is taken to be small. Starting with Equation 1.35, making assumptions 1.37 and 1.38, and recognizing that the problem is spherically symmetric, yields

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Phi_j^0}{\partial r} \right) = -\frac{e}{\varepsilon} \left( \frac{z_g n_g}{k_B T} \exp \left( -\frac{z_g e \Phi_j^0}{k_B T} \right) + \frac{z_h n_h}{k_B T} \exp \left( -\frac{z_h e \Phi_j^0}{k_B T} \right) \right). \tag{1.43}
\]

The boundary conditions for Equation 1.42 are

\[
\begin{align*}
\frac{\partial \Phi_j^0}{\partial r} \bigg|_{r=a} &= -\frac{z_i e}{4\pi \varepsilon a^2} \tag{1.44} \\
\Phi_j^0 \bigg|_{r=\infty} &= 0. \tag{1.45}
\end{align*}
\]

In Equation 1.44 a is the distance of closest approach of an ion pair. All ion pairs are assumed to have the same distance of closest approach. The first boundary condition comes from applying Gauss's law to the central charge. The second boundary condition is setting the arbitrary zero of potential.

The system has three characteristic lengths:

\[
\lambda = \sqrt{\frac{\varepsilon k_B T}{e^2 \left( z_g^2 n_g + z_h^2 n_h \right)}}, \tag{1.46}
\]

\[
\ell = -\frac{z_i z_j e^2}{8\pi \varepsilon k_B T}, \tag{1.47}
\]

and

\[
a. \tag{1.48}
\]

Equation 1.46 defines the Debye length. The Debye length is the characteristic length over which the potential decays. Equation 1.47 defines the Bjerrum length. The Bjerrum length is the distance at which the potential energy of the ion pair of ions i and j is \(2k_B T\). For the problem of interest, \(a \ll \lambda\).

Equation 1.43 can be made dimensionless with the following dimensionless variables and parameters

\[
\zeta = \frac{r}{\ell}, \tag{1.49}
\]

\[
\zeta. \tag{1.48}
\]
\[
\alpha = \frac{a}{\ell'}
\]

\[
\Phi_j = \frac{z_i e \Phi_j^0}{kT \ell'},
\]

\[
\gamma = \frac{\lambda'}{z_i},
\]

\[
\theta_g = \frac{z_g}{z_i},
\]

and

\[
\theta_h = \frac{z_h}{z_i}.
\]

By substituting Equations 1.49 through 1.54 into Equation 1.43 and making use of electroneutrality, \(0 = z_g n_g + z_h n_h\), the governing equation becomes

\[
\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left( \zeta^2 \frac{\partial \Phi_j}{\partial \zeta} \right) = \frac{\gamma^2}{\theta_h - \theta_g} \left( \exp(-\theta_g \Phi_j) - \exp(-\theta_h \Phi_j) \right). \tag{1.55}
\]

The boundary conditions become

\[
\frac{\partial \Phi_j}{\partial \zeta} \bigg|_{\zeta=\alpha} = \frac{2}{\alpha^2}
\]

and

\[
\Phi_j \bigg|_{\zeta=\infty} = 0. \tag{1.57}
\]

To obtain a singular-perturbation solution to this problem, Equation 1.55 is written for inner and outer regions. In the outer region, scaled position will be given by \(\zeta\). The potential in the outer region is given by \(\tilde{\Phi}_j\). The position is scaled as

\[
\zeta = \gamma \zeta' \sim O(1). \tag{1.58}
\]

The governing equation for the outer region is then

\[
\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left( \zeta^2 \frac{\partial \tilde{\Phi}_j}{\partial \zeta} \right) = \frac{1}{\theta_h - \theta_g} \left( \exp(-\theta_g \tilde{\Phi}_j) - \exp(-\theta_h \tilde{\Phi}_j) \right). \tag{1.59}
\]

The boundary condition that applies to the outer region is at \(\zeta = \infty\). This boundary condition becomes

\[
\tilde{\Phi}_j \bigg|_{\zeta=\infty} = 0. \tag{1.60}
\]

The potential is expanded as a series of functions of \(\gamma\) multiplied by functions \(\zeta\). The small parameter in the problem is \(\gamma\). The functions of \(\zeta\) are each taken to be of order 1. The series expansion is then

\[
\tilde{\Phi}_j(\zeta) = \tilde{\Phi}^{(0)}_j(\zeta) + \gamma \tilde{\Phi}^{(1)}_j(\zeta) + \gamma^2 \tilde{\Phi}^{(2)}_j(\zeta) + \cdots. \tag{1.61}
\]

In the inner region, the scaled position is given by \(\bar{\zeta}\), and the potential in the inner region is given by \(\bar{\Phi}_j\). The position is scaled as

\[
\bar{\zeta} = \zeta' \sim O(1). \tag{1.62}
\]

The governing equation for the inner region is then

\[
\frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \bar{\Phi}_j}{\partial \bar{\zeta}} \right) = \frac{\gamma^2}{\theta_h - \theta_g} \left( \exp(-\theta_g \bar{\Phi}_j) - \exp(-\theta_h \bar{\Phi}_j) \right). \tag{1.63}
\]

The boundary condition for the inner region is the boundary condition at \(\zeta = \alpha\). This boundary condition becomes
The potential is expanded as a series of functions of $\gamma$ multiplied by functions $\bar{\zeta}$ where $\gamma$ is the small parameter. The functions of $\bar{\zeta}$ are each taken to be of order 1. The series expansion is then

$$\bar{\Phi}_j(\bar{\zeta}) = \bar{G}^{(0)}(\gamma)\bar{\Phi}_j^{(0)}(\bar{\zeta}) + \bar{G}^{(1)}(\gamma)\bar{\Phi}_j^{(1)}(\bar{\zeta}) + \bar{G}^{(2)}(\gamma)\bar{\Phi}_j^{(2)}(\bar{\zeta}) + \cdots. \quad (1.65)$$

The first term in the outer solution is determined first. Due to the boundary condition at infinity, $\bar{\Phi}_j$ is small. Since each of the functions of $\bar{\zeta}$ is of order 1, each $G^{(r)}(\gamma)$ must be small.

Therefore, the assumption that $\bar{G}^{(0)}(\gamma) = \gamma$ is made. Substitution into the governing equation yields

$$\frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \bar{\Phi}_j^{(0)}}{\partial \bar{\zeta}} \right) = \frac{1}{\theta_h - \theta_g} \left( \exp(-\theta_g \gamma \bar{\Phi}_j^{(0)}) - \exp(-\theta_h \gamma \bar{\Phi}_j^{(0)}) \right). \quad (1.66)$$

Since $\gamma$ is small, the exponentials can be expanded in a series. Collecting terms of order $\gamma$ yields

$$\frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \bar{\Phi}_j^{(0)}}{\partial \bar{\zeta}} \right) = \bar{\Phi}_j^{(0)}. \quad (1.67)$$

Equation 1.67 can be solved using the boundary condition that $\bar{\Phi}_j^{(0)}|_{\bar{\zeta} = \infty} = 0$ to yield

$$\bar{\Phi}_j^{(0)} = \frac{\bar{c}_1^{(0)}}{\bar{\zeta}} \exp(-\bar{\zeta}), \quad (1.68)$$

where $\bar{c}_1^{(0)}$ is a constant to be determined by matching.

The first term in the inner solution is now determined. Since it is expected that $\bar{\Phi}_j = O(1)$, the assumption is that $\bar{G}^{(0)} = 1$. Substitution into the governing equation yields

$$\frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \bar{\Phi}_j^{(0)}}{\partial \bar{\zeta}} \right) = \frac{\gamma^2}{\theta_h - \theta_g} \left( \exp(-\theta_g \gamma \bar{\Phi}_j^{(0)}) - \exp(-\theta_h \gamma \bar{\Phi}_j^{(0)}) \right). \quad (1.69)$$

Since $\gamma$ is small, terms of order 1 can be collected to obtain

$$\frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \bar{\Phi}_j^{(0)}}{\partial \bar{\zeta}} \right) = 0. \quad (1.70)$$

Solving this Equation with the boundary condition

$$\left. \frac{\partial \bar{\Phi}_j^{(0)}}{\partial \bar{\zeta}} \right|_{\bar{\zeta} = \alpha} = \frac{2}{\alpha^2}, \quad (1.71)$$

yields

$$\bar{\Phi}_j^{(0)} = -\frac{2}{\bar{\zeta}} + \bar{c}_2^{(0)}, \quad (1.72)$$

where $\bar{c}_2^{(0)}$ is a constant to be determined from matching.

The first terms of the outer solution and the inner solution can now be matched. In terms of $\zeta$, the outer and inner solutions are

$$\bar{\Phi}_j = \frac{\bar{c}_1^{(0)}}{\zeta} \exp(-\gamma \zeta) + \cdots \quad (1.73)$$
and
\[
\bar{\phi}_j = -\frac{2}{\zeta} + \bar{c}_2^{(0)} + \ldots.
\]  
(1.74)

Matching the outer and inner solutions asymptotically yields \( \bar{c}_1^{(0)} = -2 \), and \( \bar{c}_2^{(0)} = 0 \).

To introduce the next term, the next highest order of approximation must be determined. There are three different places where the next term can arise: matching the inner and outer expansions, the boundary conditions, or the governing equation. From matching the outer and the inner solutions, the outer solution has a term of order \( \gamma \) that the inner solution does not have. The boundary conditions are satisfied by the inner and outer solutions, so they do not contain additional terms. In the governing equation the neglected terms are of order \( \gamma^2 \).

Thus, the next term is of order \( \gamma \). Since the next term is of order \( \gamma \), then for the outer solution \( \bar{G}^{(1)} = \gamma^2 \) and for the inner solution \( \bar{G}^{(1)} = \gamma \).

For the second term in the outer solution \( \bar{\phi}^{(1)}_j = \gamma^2 \). The potential is then given by
\[
\bar{\phi}_j = -\frac{2}{\zeta} + \gamma^2 \bar{\phi}^{(1)}_j + \ldots.
\]
(1.75)

Inserting this into the governing equation and collecting terms of order \( \gamma^2 \) yields
\[
\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left( \zeta^2 \frac{\partial \bar{\phi}^{(1)}_j}{\partial \zeta} \right) = \bar{\phi}^{(1)}_j - \left( \theta_g + \theta_h \right) \frac{2}{\zeta^2} \exp(-2\zeta) \tag{1.76}
\]

The solution satisfying the boundary condition that \( \bar{\phi}^{(1)}_j \big|_{\zeta=\infty} = 0 \) is
\[
\bar{\phi}^{(1)}_j = \frac{1}{\zeta} \exp(-\zeta) \frac{\theta_g^2 - \theta_h^2}{\theta_h - \theta_g} \left( \exp(2\zeta) \text{Ei}(-3\zeta) - \text{Ei}(-\zeta) \right)
\]
\[-\frac{2}{\zeta} \exp(-\zeta) \bar{c}_2^{(1)}, \tag{1.77}
\]

where \( \text{Ei} \) is the exponential integral and the constant \( \bar{c}_2^{(1)} \) will be determined by matching with the inner solution. The exponential integral is defined as \( \text{Ei}(x) = \int_{-\infty}^{x} t^{-1} \exp(t) \, dt \).

For the second term in the inner solution \( \bar{G}^{(1)} = \gamma \). The potential is then
\[
\bar{\phi}_j = -\frac{2}{\zeta} + \gamma \bar{\phi}^{(1)}_j + \ldots. \tag{1.78}
\]

Inserting this into the governing equation and collecting terms of order \( \gamma \) yields
\[
\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left( \zeta^2 \frac{\partial \bar{\phi}^{(1)}_j}{\partial \zeta} \right) = 0. \tag{1.79}
\]

The solution satisfying the boundary condition
\[
\frac{\partial \bar{\phi}^{(1)}_j}{\partial \zeta} \bigg|_{\zeta=\alpha} = 0; \tag{1.80}
\]

is
\[
\bar{\phi}^{(1)}_j = \bar{c}_2^{(1)}, \tag{1.81}
\]

where the constant \( \bar{c}_2^{(1)} \) is to be determined by matching with the inner solution.

The second terms of the inner and outer solutions can now be matched. In terms of \( \zeta \), the outer and inner solutions are
\( \tilde{\Phi}^{(1)} = -\frac{1}{\gamma \zeta} \exp(-\gamma \zeta) (\theta_g + \theta_h)(\exp(2\gamma \zeta) \text{Ei}(-3\gamma \zeta) - \text{Ei}(-\gamma \zeta)) \) 
\( - \frac{2}{\gamma \zeta} \exp(-\gamma \zeta) \tilde{c}^{(1)}_2 \) \hfill (1.82)

and

\( \bar{\Phi}_j = -\frac{2}{\zeta} + \gamma \bar{c}^{(1)}_2 + \ldots. \) \hfill (1.83)

Expanding the outer solution for small \( \gamma \), keeping terms of order \( \gamma \) yields

\( \tilde{\Phi}_j = -\frac{2}{\zeta} + 2\gamma - \frac{\gamma}{\zeta} (\theta_g + \theta_h) \ln(3) - \frac{2\gamma}{\zeta} \bar{c}^{(1)}_2 + \ldots \) \hfill (1.84)

Matching the inner and outer solutions yields

\( \bar{c}^{(1)}_2 = -\frac{1}{2} (\theta_g + \theta_h) \ln(3) \) \hfill (1.85)

and

\( \bar{c}^{(1)}_2 = 2 \) \hfill (1.86)

The inner and outer solutions are now

\( \tilde{\Phi}_j = -\frac{2}{\zeta} \exp(-\gamma \zeta) \)
\( + \frac{\gamma}{\zeta} \exp(-\gamma \zeta) (\theta_g + \theta_h) \ln(3) - \exp(2\gamma \zeta) \text{Ei}(-3\gamma \zeta) + \ldots \) \hfill (1.87)

and

\( \bar{\Phi}_j = -\frac{2}{\zeta} + 2\gamma + \ldots. \) \hfill (1.88)

To introduce the next term, the next highest order of approximation is determined. Expanding the outer solution for small \( \zeta \), the lowest order term that is unmatched by the inner solution is of order \( \gamma^2 \ln(\gamma) \). Since the boundary conditions are satisfied by the inner and outer solutions, they do not produce additional terms. In the governing equation, terms of order \( \gamma^2 \) have been neglected. The next term is then \( O(\gamma^2 \ln(\gamma)) \).

For the outer solution, then \( \tilde{G}^{(2)} = \gamma^3 \ln(\gamma) \). The potential is expressed as

\( \tilde{\Phi}_j(\bar{\zeta}) = -\frac{2\gamma}{\zeta} \exp(-\bar{\zeta}) \)
\( + \frac{\gamma^2}{\zeta} \exp(-\bar{\zeta}) (\theta_g + \theta_h)(\ln(3) - \exp(2\bar{\zeta}) \text{Ei}(-3\bar{\zeta}) \ldots \) \hfill (1.89)

Inserting this into the governing equation and collecting terms of order \( \gamma^3 \ln(\gamma) \) yields

\( \frac{1}{\bar{\zeta}^2} \frac{\partial}{\partial \bar{\zeta}} \left( \bar{\zeta}^2 \frac{\partial \tilde{\Phi}_j^{(2)}}{\partial \bar{\zeta}} \right) = \tilde{\Phi}_j^{(2)}. \) \hfill (1.90)

Solving this Equation, making use of the boundary condition that \( \tilde{\Phi}_j^{(2)}|_{\bar{\zeta}=\infty} = 0 \), yields

\( \tilde{\Phi}_j^{(2)} = \frac{\bar{c}_1^{(2)}}{\bar{\zeta}} \exp(-\bar{\zeta}). \) \hfill (1.91)
where $\tilde{c}_1^{(2)}$ is a constant to be determined by matching.

For the inner solution, $G^{(2)} = \gamma^2 \ln(\gamma)$. The expression for the potential is then

$$\bar{\phi}_j = -\frac{2}{\zeta} + 2\gamma + \gamma^2 \ln(\gamma) \bar{\phi}_j^{(2)} + \ldots. \quad (1.92)$$

Inserting this into the governing equation and collecting terms of order $\gamma^2 \ln(\gamma)$ yields

$$\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left( \zeta^2 \frac{\partial \bar{\phi}_j^{(2)}}{\partial \zeta} \right) = 0. \quad (1.93)$$

Solving this Equation with the boundary condition

$$\frac{\partial \bar{\phi}_j^{(2)}}{\partial \zeta} \bigg|_{\zeta=\alpha} = 0, \quad (1.94)$$

yields

$$\bar{\phi}_j^{(2)} = \tilde{c}_2^{(2)}. \quad (1.95)$$

The inner and outer solutions can now be matched. In terms of $\zeta$, the outer and inner solutions are

$$\bar{\phi}_j = -\frac{2}{\zeta} \exp(-\gamma\zeta) + \frac{\gamma}{\zeta} \exp(-\gamma\zeta) \left( \theta_g + \theta_h \right) (\ln(3) - \exp(2\gamma\zeta) \text{Ei}(-3\gamma\zeta) + \ldots \quad (1.96)$$

and

$$\bar{\phi}_j = -\frac{2}{\zeta} + 2\gamma + \gamma^2 \ln(\gamma) \tilde{c}_1^{(2)} \exp(-\gamma\zeta) + \ldots \quad (1.97)$$

Expanding the outer solution for small $\gamma$, keeping terms of order $\gamma^2 \ln(\gamma)$ yields

$$\bar{\phi}_j = -\frac{2}{\zeta} + 2\gamma - 2\gamma^2 \ln(\gamma) \left( \theta_g + \theta_h \right) + \gamma^2 \ln(\gamma) \frac{\tilde{c}_1^{(2)}}{\zeta} \exp(-\gamma\zeta) + \ldots \quad (1.98)$$

and

$$\bar{\phi}_j = -\frac{2}{\zeta} + 2\gamma + \gamma^2 \ln(\gamma) \tilde{c}_2^{(2)} + \ldots. \quad (1.99)$$

Matching yields

$$\tilde{c}_1^{(2)} = 0 \quad (1.100)$$

and

$$\tilde{c}_2^{(2)} = -2(\theta_g + \theta_h). \quad (1.101)$$

The inner and outer solutions are then

$$\bar{\phi}_j = -\frac{2}{\zeta} \exp(-\gamma\zeta) + \frac{\gamma}{\zeta} \exp(-\gamma\zeta) \left( \theta_g + \theta_h \right) (\ln(3) - \exp(2\gamma\zeta) \text{Ei}(-3\gamma\zeta) + \ldots \quad (1.102)$$

and
\[ \phi_j = -\frac{2}{\zeta} + 2\gamma - 2\gamma^2 \ln(\gamma) \left( \theta_g + \theta_h \right) + \ldots \]  

(1.103)

Higher order terms can also be calculated; however, the above terms are sufficient for the purpose of interest.

The composite solution to \( O(\gamma^2 \ln(\gamma)) \) is then given by

\[
\phi_j = -\frac{2}{\zeta} \exp(-\gamma \zeta) \\
+ \frac{\gamma}{\zeta} \exp(-\gamma \zeta) \left( \theta_g + \theta_h \right) \ln(3) - \exp(2\gamma \zeta) \text{Ei}(-3\gamma \zeta) \\
+ \text{Ei}(-\gamma \zeta).
\]  

(1.104)

It is interesting to consider whether the composite solution matches the boundary conditions. The composite solution matches the outer boundary condition. However, the composite solution only matches the inner boundary condition to \( O(\gamma^2 \ln(\gamma)) \).

For the purpose of calculating the recombination rate constant, only terms up to \( O(\gamma) \) are used. Keeping terms of order \( \gamma \), the composite solution is

\[
\phi_j = -\frac{2}{\zeta} \exp(-\gamma \zeta).
\]  

(1.105)

In dimensional form, the expression for the potential is

\[
\Phi_j^0 = -\frac{k_B T \ell_2 \ell}{z_i e r} \exp \left( -\frac{r}{\lambda} \right).
\]  

(1.106)

The distribution functions are determined by combining the Boltzmann distributions given by Equations 1.25 and 1.26, the potential energies given by Equations 1.37 and 1.38, and the potential given by 1.106. The distribution functions are

\[
\frac{n_{jg}^0}{n_j n_g} = \exp \left( \frac{z_g}{z_i} \frac{2 \ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right), \quad (1.107)
\]

and

\[
\frac{n_{jh}^0}{n_j n_h} = \exp \left( \frac{z_h}{z_i} \frac{2 \ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right). \quad (1.108)
\]

Equations 1.107 and 1.108 are plotted in Figure 2. Figure 2 clearly shows the ion cloud formed around an ion of type \( j \). There is an excess of ions of type \( g \) and a depletion of ions of type \( h \).

In a similar manner, the potential in the vicinity of an ion of type \( i \) can be derived. The resulting Equation for the potential is

\[
\Phi_i^0 = -\frac{k_B T \ell_2 \ell}{z_i e r} \exp \left( -\frac{r}{\lambda} \right). \quad (1.109)
\]
Figure 1.2. The normalized distribution function as a function of position. Equations 1.107 and 1.108 are plotted for the conditions of $z_i = 1$, $z_j = -1$, $z_g = 1$, $z_h = -1$, with 0.1 M supporting electrolyte. The characteristic lengths are $\ell = 0.36$ nm, $\lambda = 0.96$ nm, and $a = 0.4$ nm.

Distribution Function during Recombination

The expression for the distribution function during the recombination of ions can now be derived. The ions are moving following Nernst-Planck expressions. In the last section, the electrostatic potential surrounding the ions was determined. Using this electrostatic potential,
the distribution function during recombination will be determined. The distribution function will then be used to determine the rate of recombination.

With the same assumption of Debye and Hückel, the potential energy is given by
\[
U_{ij} = U_{ji} = z_j e \Phi_i^0 = z_i e \Phi_j^0.
\] (1.110)

Combining Equation 1.110 for the potential energy with Equation 1.106 for the electrostatic potential and Equation 1.24 for the velocity difference leads to
\[
\mathbf{v}_{ji} - \mathbf{v}_{ij} = -(D_i + D_j) \nabla \left( \ln f_{ji} - \frac{2\ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right)
\] (1.111)

Equation 1.111 for the velocity difference is combined with Equation 1.16 for the continuity of the distribution function to yield
\[
\frac{\partial f_{ji}}{\partial t} = -(D_i + D_j) \nabla \cdot \left( -\nabla f_{ji} + f_{ji} \nabla \frac{2\ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right).
\] (1.112)

Equation 1.112 is the continuity expression governing the distribution function. Equation 1.112 is solved to determine the rate of collision of ions and thus the rate of recombination. The Equation is solved under steady-state conditions so that Equation 1.112 becomes
\[
0 = -(D_i + D_j) \nabla \cdot \left( -\nabla f_{ji} + f_{ji} \nabla \frac{2\ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right).
\] (1.113)

Since the distribution function is spherically symmetric, Equation 1.113 reduces to
\[
0 = \frac{\partial^2 f_{ji}}{\partial r^2} + \left( \frac{2}{r} + \frac{2\ell}{r^2} \exp \left( -\frac{r}{\lambda} \right) \left( 1 + \frac{r}{\lambda} \right) \right) \frac{\partial f_{ji}}{\partial r} - f_{ji} \frac{2\ell}{\lambda^2 r} \exp \left( -\frac{r}{\lambda} \right).
\] (1.114)

The boundary conditions are
\[
f_{ji} \bigg|_{r=a} = 0 \tag{1.115}
\]
and
\[
f_{ji} \bigg|_{r=\infty} = n_i n_j. \tag{1.116}
\]

The boundary condition given by Equation 1.115 is due to the ions reacting when they reach a separation of \( r = a \). The boundary condition given by Equation 1.116 is that the positions of the ions are uncorrelated as \( r \to \infty \).

The solution of Equation 1.114 can be related to the recombination rate using the divergence theorem. Using the divergence theorem, Equation 1.112 becomes
\[
\int \frac{\partial f_{ji}}{\partial t} dV = \oint \left( D_i + D_j \right) \left( \nabla f_{ji} - f_{ji} \nabla \frac{2\ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right) \cdot \mathbf{n} dS. \tag{1.117}
\]

The right side of Equation 1.117 is the flux of ions into a surface. If the surface of interest is a sphere at \( r = a \) then the right side is the rate of recombination of ions. Comparing the macroscopic material balance, Equation 1.3, to Equation 1.117 yields
\[
k_{-1} n_i n_j = \oint \left( D_i + D_j \right) \left( \nabla f_{ji} - f_{ji} \nabla \frac{2\ell}{r} \exp \left( -\frac{r}{\lambda} \right) \right) \cdot \mathbf{n} dS. \tag{1.118}
\]

Evaluating the surface integral at \( r = a \), recognizing the boundary condition given by Equation 1.115, and making use of spherical symmetry yields
\[
k_{-1} n_i n_j = 4\pi a^2 \left( D_i + D_j \right) \frac{df_{ji}}{dr} \bigg|_{r=a}. \tag{1.119}
\]
Solving Equation 1.114 with boundary conditions of Equation 1.115 and Equation 1.116 yields the distribution function during recombination. Equation 1.118 relates this distribution function to the recombination rate constant.

In order to solve Equation 1.114 more easily, the expression is rewritten using
\[ \zeta = \frac{r}{\ell}, \] (1.120)
\[ \alpha = \frac{a}{\ell}, \] (1.121)
\[ F = \frac{f_{ji}}{n_i n_j}, \] (1.122)
and
\[ \gamma = \frac{\ell}{\lambda}. \] (1.123)

The governing equation for the distribution function is then
\[ 0 = \frac{d^2 F}{d \zeta^2} + \left( \frac{2}{\zeta} + \frac{2}{\zeta^2} \exp(-\gamma \zeta) (1 + \gamma \zeta) \right) \frac{dF}{d \zeta} - \frac{2}{\zeta} \gamma^2 \exp(-\gamma \zeta), \] (1.124)
with boundary conditions
\[ F|_{\zeta=\alpha} = 0 \] (1.125)
and
\[ F|_{\zeta=\infty} = 1. \] (1.126)

Two different solutions to Equation 1.124 were calculated: a numerical solution and a singular-perturbation solution.

**Numerical Solution for the Distribution Function**

The governing equation for the distribution function can be solved by approximating the expression using finite-difference expressions and solving the resulting linear algebraic equations using BAND. To deal with the boundary condition at infinity, the problem is rescaled using the variable
\[ \sigma = \frac{1}{\zeta}. \] (1.127)

The governing equation for the distribution function is then
\[ 0 = \frac{d^2 F}{d \sigma^2} - 2 \exp \left( -\frac{\gamma}{\sigma} \right) \left( 1 + \frac{\gamma}{\sigma} \right) \frac{dF}{d \sigma} - \frac{2}{\sigma^3} \gamma^2 \exp \left( -\frac{\gamma}{\sigma} \right), \] (1.128)
with boundary conditions
\[ F|_{\sigma=\alpha^{-1}} = 0 \] (1.129)
and
\[ F|_{\sigma=0} = 1. \] (1.130)

Equation 1.127 is valid for small \( \gamma \). For \( \gamma = 0 \), Equation 1.128 reduces to
\[ 0 = \frac{d^2 F}{d \sigma^2} - 2 \frac{dF}{d \sigma}, \] (1.131)
The solution to this expression satisfying the boundary conditions will be denoted by \( F_0 \) where
\[ F_0 = \frac{1}{1 - \exp \left( \frac{2 \gamma}{\alpha} \right) \left( \exp(2\sigma) - \exp \left( \frac{2}{\alpha} \right) \right)}. \] (1.132)
The governing equation can now be rewritten in terms of a deviation variable $F'$ where
\[ F = F_0 + F'. \tag{1.133} \]
Introduction of the deviation variable into Equation 1.128 leads to
\[
0 = \frac{d^2F'}{d\sigma^2} - 2 \exp\left(-\frac{\gamma}{\sigma}\right) \left(1 + \frac{\gamma}{\sigma}\right) \frac{dF'}{d\sigma} - F' \frac{2 \gamma^2}{\sigma^3} \exp\left(-\frac{\gamma}{\sigma}\right) \\
+ \frac{1}{1 - \exp\left(\frac{2\gamma}{\alpha}\right)} \left(1 - \exp\left(-\frac{\gamma}{\sigma}\right) \left(1 + \frac{\gamma}{\sigma}\right)\right) 4 \exp(2\sigma) \\
+ \left(\exp\left(\frac{2\gamma}{\alpha}\right) - \exp(2\sigma)\right) \frac{2\gamma^2}{\sigma^3} \exp\left(-\frac{\gamma}{\sigma}\right). \tag{1.134} \]
with boundary conditions
\[ F'|_{\sigma=\alpha^{-1}} = 0 \tag{1.135} \]
and
\[ F'|_{\sigma=0} = 0. \tag{1.136} \]
Equation 1.134 was solved numerically using finite differences. Fortran code for this solution is in Appendix 1.1.

**Singular-Perturbation Solution for the Distribution Function**

Since the parameter $\gamma$ is small, the governing equation can be solved as a perturbation solution in $\gamma$. A regular-perturbation solution to the Equation is not valid because at large $\zeta$, $F = O(1)$, while for $\zeta \sim \alpha$, $F$ is small. Therefore, Equation 1.124 will be solved as a singular-perturbation problem.

In the outer region, scaled position is $\bar{\zeta}$. The distribution function in the outer region is called $\bar{F}$. The scaled variables are
\[ \bar{\zeta} = \gamma \zeta \sim O(1) \tag{1.137} \]
and
\[ \bar{F} = F \sim O(1). \tag{1.138} \]
The governing equation for the outer region is then
\[
0 = \frac{d^2\bar{F}}{d\bar{\zeta}^2} + \left(\frac{2}{\bar{\zeta}} + \frac{2\gamma}{\bar{\zeta}^2} \exp(-\bar{\zeta}) \left(1 + \bar{\zeta}\right)\right) \frac{d\bar{F}}{d\bar{\zeta}} - \bar{F} \frac{2\gamma}{\bar{\zeta}} \exp(-\bar{\zeta}). \tag{1.139} \]
The boundary condition that applies to the outer region is where $\zeta \to \infty$. This boundary condition becomes
\[ \bar{F}|_{\bar{\zeta} \to \infty} = 1. \tag{1.140} \]
The distribution function is now expanded as a series of functions of $\gamma$ multiplied by functions $\bar{\zeta}$. The parameter $\gamma$ is taken to be small. The functions of $\bar{\zeta}$ are each taken to be of order 1. The series expansion is then
\[ \bar{F}(\bar{\zeta}) = \bar{G}^{(0)}(\gamma) \bar{F}^{(0)}(\bar{\zeta}) + \bar{G}^{(1)}(\gamma) \bar{F}^{(1)}(\bar{\zeta}) + \bar{G}^{(2)}(\gamma) \bar{F}^{(2)}(\bar{\zeta}) + \ldots. \tag{1.141} \]
In the inner region, the scaled position is given by $\bar{\zeta}$, and the distribution function in the inner region is called $\bar{F}$. The scaled variables are
\[ \bar{\zeta} = \bar{\zeta} \sim O(1) \tag{1.142} \]
and
\[ \bar{F} = F \sim \text{small}. \tag{1.143} \]
The governing equation for the inner region is then
\[ 0 = \frac{d^2 \bar{F}}{d \bar{\zeta}^2} + \left( \frac{2}{\bar{\zeta}} + \frac{2}{\bar{\zeta}^2} \exp(-\gamma \bar{\zeta}) (1 + \gamma \bar{\zeta}) \right) \frac{d \bar{F}}{d \bar{\zeta}} - \bar{F} \frac{2}{\bar{\zeta}} \gamma^2 \exp(-\gamma \bar{\zeta}). \] (1.144)

The boundary condition for the inner region is the boundary condition at \( \zeta = \alpha \). This boundary condition becomes
\[ \bar{F} \big|_{\zeta=\alpha} = 0 \] (1.145)

The distribution function is now expanded as a series of functions of \( \gamma \) multiplied by functions \( \bar{\zeta} \). The parameter \( \gamma \) is taken to be small. The functions of \( \bar{\zeta} \) are each taken to be of order 1. The series expansion is then
\[ \bar{F} (\bar{\zeta}) = \bar{G}^{(0)} (\gamma) \bar{F}^{(0)} (\bar{\zeta}) + \bar{G}^{(1)} (\gamma) \bar{F}^{(1)} (\bar{\zeta}) + \bar{G}^{(2)} (\gamma) \bar{F}^{(2)} (\bar{\zeta}) + \ldots. \] (1.146)

For the first term in the outer solution, due to the boundary condition at infinity, \( \bar{F} = O(1) \). Since each of the functions of \( \bar{\zeta} \) is of order 1, it is assumed that \( \bar{G}^{(0)} (\gamma) = 1 \).

Substitution into the governing equation yields
\[ 0 = \frac{d^2 \bar{F}^{(0)}}{d \bar{\zeta}^2} + \left( \frac{2}{\bar{\zeta}} + \frac{2 \gamma}{\bar{\zeta}^2} \exp(-\gamma \bar{\zeta}) (1 + \bar{\zeta}) \right) \frac{d \bar{F}^{(0)}}{d \bar{\zeta}} - \bar{F}^{(0)} \frac{2 \gamma}{\bar{\zeta}} \exp(-\gamma \bar{\zeta}). \] (1.147)

Collecting terms of order 1 yields
\[ 0 = \frac{d^2 \bar{F}^{(0)}}{d \bar{\zeta}^2} + \frac{2}{\bar{\zeta}} \frac{d \bar{F}^{(0)}}{d \bar{\zeta}} + \frac{2 \gamma}{\bar{\zeta}^2} \frac{d \bar{F}^{(0)}}{d \bar{\zeta}}. \] (1.148)

The solution satisfying the boundary condition that \( \bar{F}^{(0)} \big|_{\zeta=\infty} = 1 \) is
\[ \bar{F}^{(0)} = 1 - \frac{\bar{c}_1^{(0)}}{\bar{\zeta}}, \] (1.149)

where \( \bar{c}_1^{(0)} \) is a constant to be determined by matching.

Since the first term of the inner solution is small, the assumption is that \( \bar{G}^{(0)} = 1 \).

Substitution into the governing equation yields
\[ 0 = \frac{d^2 \bar{F}^{(0)}}{d \bar{\zeta}^2} + \left( \frac{2}{\bar{\zeta}} + \frac{2}{\bar{\zeta}^2} \exp(-\gamma \bar{\zeta}) (1 + \gamma \bar{\zeta}) \right) \frac{d \bar{F}^{(0)}}{d \bar{\zeta}} - \bar{F}^{(0)} \frac{2}{\bar{\zeta}} \gamma^2 \exp(-\gamma \bar{\zeta}). \] (1.150)

Collecting terms of order 1 yields
\[ 0 = \frac{d^2 \bar{F}^{(0)}}{d \bar{\zeta}^2} + \left( \frac{2}{\bar{\zeta}} + \frac{2}{\bar{\zeta}^2} \right) \frac{d \bar{F}^{(0)}}{d \bar{\zeta}}. \] (1.151)

The solution satisfying the boundary condition \( \bar{F}^{(0)} \big|_{\zeta=\alpha} = 0 \) is
\[ \bar{F}^{(0)} = \bar{c}_1^{(0)} \left( \exp \left( \frac{2}{\bar{\zeta}} \right) - \exp \left( \frac{2}{\alpha} \right) \right). \] (1.152)

where \( \bar{c}_1^{(0)} \) is a constant to be determined from matching.

To match the outer and inner solutions, the expressions are rewritten in terms of \( \zeta \) as
\[ \bar{F} = 1 - \frac{\bar{c}_1^{(0)}}{\gamma \zeta} + \ldots \] (1.153)

and
\[ \bar{F} = \bar{c}_1^{(0)} \left( \exp \left( \frac{2}{\bar{\zeta}} \right) - \exp \left( \frac{2}{\alpha} \right) \right) + \ldots. \] (1.154)
Matching the two solutions yields
\begin{equation}
\bar{c}_1^{(0)} = 0
\end{equation}
and
\begin{equation}
\bar{c}_1^{(0)} = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)}.
\end{equation}

The outer and inner solutions are then
\begin{equation}
\bar{F} = 1 + \ldots
\end{equation}

and
\begin{equation}
\bar{F} = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left(\exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right)\right) + \ldots.
\end{equation}

The next term is determined by the next highest order of approximation. There are no unmatched terms in the inner and outer solutions. The boundary conditions are satisfied by the inner and outer solutions, and therefore do not generate additional terms. In the governing equation, terms of order $\gamma$ have been neglected. The next term is then $O(\gamma)$.

For the outer solution, then $\bar{G}^{(1)} = \gamma$. The distribution function is then
\begin{equation}
\bar{F} = 1 + \gamma \bar{F}^{(1)} + \ldots.
\end{equation}

Substitution into the governing equation and collecting terms of order $\gamma$ yields
\begin{equation}
0 = \frac{d^2 \bar{F}^{(1)}}{d\bar{\zeta}^2} + \frac{2}{\bar{\zeta}} \frac{d\bar{F}^{(1)}}{d\bar{\zeta}} - \frac{2}{\bar{\zeta}} \exp(-\bar{\zeta}).
\end{equation}

Solving this Equation, making use of the boundary condition that $\bar{F}^{(1)}|_{\bar{\zeta} = \alpha} = 0$, yields
\begin{equation}
\bar{F}^{(1)} = \frac{2}{\bar{\zeta}} \exp(-\bar{\zeta}) - \frac{\bar{c}_1^{(1)}}{\bar{\zeta}},
\end{equation}

where $\bar{c}_1^{(1)}$ is a constant to be determined by matching with the inner solution.

For the inner solution, $\bar{G}^{(0)} = \gamma$. The distribution function is then
\begin{equation}
\bar{F} = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left(\exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right)\right) + \gamma \bar{F}^{(1)} + \ldots.
\end{equation}

Substitution into the governing equation and collecting terms of order $\gamma$ yields
\begin{equation}
0 = \frac{d^2 \bar{F}^{(1)}}{d\zeta^2} + \left(\frac{2}{\zeta} + \frac{2}{\zeta^2}\right) \frac{d\bar{F}^{(1)}}{d\zeta}.
\end{equation}

Solving this Equation using the boundary condition $\bar{F}^{(1)}|_{\zeta = \alpha} = 0$, yields
\begin{equation}
\bar{F}^{(1)} = \bar{c}_1^{(1)} \left(\exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right)\right),
\end{equation}

where $\bar{c}_1^{(1)}$ is a constant to be determined by matching with the outer solution.

The inner and outer solutions can now be matched. In terms of $\zeta$, the outer and inner solutions are
\begin{equation}
\bar{F} = 1 + \frac{2}{\zeta} \exp(-\gamma \zeta) - \frac{\bar{c}_1^{(1)}}{\zeta} \ldots
\end{equation}

and
\[
\bar{F} = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left( \exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right) \right) + \gamma \bar{c}_1^{(1)} \left( \exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right) \right) \ldots \tag{1.166}
\]

Matching the inner and outer solutions yields
\[
\bar{c}_1^{(1)} = 2
\tag{1.167}
\]
and
\[
\bar{c}_1^{(1)} = -\frac{2}{1 - \exp\left(\frac{2}{\alpha}\right)}.
\tag{1.168}
\]
The outer and inner solutions are then
\[
\bar{F} = 1 + \frac{2}{\zeta} \exp(-\gamma \zeta) - \frac{2}{\zeta} \ldots
\tag{1.169}
\]
and
\[
\bar{F} = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left( \exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right) \right) (1 - 2\gamma) \ldots
\tag{1.170}
\]
Thus, the composite solution is given by
\[
F = \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left( \exp\left(\frac{2}{\zeta}\right) - \exp\left(\frac{2}{\alpha}\right) \right) (1 - 2\gamma) + \frac{2}{\zeta} \exp(-\gamma \zeta) - \frac{2}{\zeta} + 2\gamma \ldots
\tag{1.171}
\]
Higher order terms can easily be calculated. However, since the potential that was used is accurate only to order \(\gamma\), further terms are not physically accurate. It is of interest to point out that the composite solution only matches the boundary condition at \(\zeta = \alpha\) to order \(\gamma\).

To compare the singular-perturbation solution to the numerical solution, the singular-perturbation solution is rewritten using Equations 1.127, 1.132, and 1.133. The singular-perturbation solution for the deviation variable is then
\[
F' = -2\gamma \frac{1}{1 - \exp\left(\frac{2}{\alpha}\right)} \left( \exp(2\sigma) - \exp\left(\frac{2}{\alpha}\right) \right) + 2\theta \exp\left(-\frac{\gamma}{\sigma}\right) - 2\sigma + 2\gamma \ldots
\tag{1.172}
\]
The numerical solution and the singular-perturbation solution are compared in Figures 3 and 4.
Figure 1.3. The numerical solution and the singular-perturbation solution for the deviation variable are compared for the case $\gamma = 0.1$ and $\alpha = 1$. 
Figure 1.4. The numerical solution and the singular-perturbation solution for the dimensionless distribution function are compared for the case $\gamma = 0.1$ and $\alpha = 1$.

Rate Constant for a Collision-Controlled Reaction

The rate constant was related to the distribution function in Equation 1.119. In terms of the dimensionless distribution function, Equation 1.119 is

$$k_{-1} = 4\pi a^2 (D_i + D_j) \frac{1}{\ell} \frac{dF}{d\zeta\mid_{\zeta=\alpha}}.$$  \hspace{1cm} (1.173)

The derivative in Equation 1.173 can be evaluated using the expression for the singular-perturbation solution. The derivative, keeping terms of order $\gamma$ is given by

$$\frac{dF}{d\zeta\mid_{\zeta=\alpha}} = -\frac{2}{\alpha^2} \frac{\exp\left(\frac{2}{\alpha}\right)}{1 - \exp\left(\frac{2}{\alpha}\right)} (1 - 2\gamma).$$  \hspace{1cm} (1.174)

The final expression for the rate constant is then
\[ k_{-1} = 4\pi(D_i + D_j)a \frac{2\ell}{a} \frac{1}{1 - \exp\left(-\frac{2\ell}{\lambda}\right)} \left(1 - \frac{2\ell}{\lambda}\right). \quad (1.175) \]

Equation 1.175 is the theoretical expression for the rate constant of a collision-controlled reaction. The expression was originally derived by Debye.² It is interesting to consider what happens to the reaction rate constant under various limits.

In the limit that the reacting ions are uncharged, \( \ell \to 0 \). In this limit the rate constant becomes

\[ k_{-1} = 4\pi(D_i + D_j)a. \quad (1.176) \]

This expression for the rate constant was first derived by Smoluchowski.⁴ Smoluchowski determined this expression while deriving the rate of coagulation of colloidal particles.

In the limit that there is no supporting electrolyte and the ions are of negligible size, \( \lambda \to \infty \) and \( a \to 0 \). In this limit the expression for the rate constant becomes

\[ k_{-1} = 8\pi(D_i + D_j)\ell \quad (1.177) \]

This expression for the rate constant was first derived by Langevin.³ Langevin derived this expression while treating the quenching of dilute plasma charges in a dense gas.

Collision controlled reactions are common in aqueous acid-base reactions.¹³ Often these reactions involve molecules that contain bulky side groups that can partially block the reactive site. To account for this effect, the Equation for the reaction rate constant can be modified to contain a geometry factor.⁷ Modifying Equation 1.175 to include a geometry factor leads to

\[ k_{-1} = \theta 4\pi(D_i + D_j)a \frac{2\ell}{a} \frac{1}{1 - \exp\left(-\frac{2\ell}{\lambda}\right)} \left(1 - \frac{2\ell}{\lambda}\right), \quad (1.178) \]

where \( \theta \) is the geometry factor. The geometry factor accounts for what happens if the molecules need a certain arrangement for the reaction to occur. The geometry factor takes values between 0 and 1.

In practice, when a recombination rate constant is of the order of the magnitude predicted by Equation 1.175, it is considered to be controlled by the collision of the reactants. The only free parameter in Equation 1.175 is \( a \). It is usually adjusted to fit the experimental measurement. However, the recombination rate constant can be increased only by changing \( a \). This can be seen in the ratio of the rate constant to the rate constant for \( a = 0 \), expressed as

\[ \frac{k_{-1}}{k_{-1}^0} = \frac{1}{1 - \exp\left(-\frac{2\ell}{a}\right)}. \quad (1.179) \]

Equation 1.179 is plotted in Figure 5.

To account for a reaction rate constant slightly smaller than that predicted by Equation 1.174, the geometry factor is used. There have been various attempts at predicting the geometry factor.⁷ These theories often introduce different unmeasured parameters and have not represented decisive steps forward. The difficulty in using the geometry factor is that it introduces a second parameter. Since the reaction rate constant is often measured at a single temperature, the result is two adjustable parameters to fit a single data point. One way to approach this difficulty is to assume that all reactions with similar mechanisms have the same \( a \).
The only adjustable parameter between reactions is then $\theta$. This fits the physical picture since one expects that reactions with similar mechanisms will react at the same distance.

Figure 1.5. The ratio of the reaction rate constants as a function of $a$. The reaction rate constant $k_{-1}^0$ is when $a = 0$. The plot is for the case when $\ell = 0.36$ nm as occurs in 1-1 electrolytes in aqueous solutions at 25 °C and 1 bar.
Conclusion

The general theoretical expression for a recombination rate constant that is controlled by the collision of the reactants is given by Equation 1.178. It was derived following the distribution function approach of Onsager and Fuoss. This method was employed because it clearly shows why $k_{-1} \propto D_i + D_j$. The distribution function was assumed to follow motion governed by a Nernst-Planck Equation. The potential used in the migration terms was treated as a coulomb potential shielded by an ion cloud. The expression for this potential is given in Equation 1.106 and Equation 1.109 and was determined by solving the Poisson-Boltzmann Equation using a singular-perturbation expansion. The continuity equation for the distribution function with this potential was then solved using two methods: numerical solution and singular-perturbation solution. The expression for the rate of recombination of reactants for the distribution function following the singular-perturbation solution was then used to determine the expression for the recombination rate constant.

Notation

- $a$: Closest distance of approach of the ions
- $D_i$: Diffusivity
- $e$: Elementary charge of a proton
- $f_{ji}$: Distribution function
- $F$: Dimensionless distribution function
- $F_0$: Dimensionless distribution function for $\lambda \to \infty$
- $F'$: Deviation of the dimensionless distribution function from that for $\lambda \to \infty$
- $k_1$: Dissociation rate constant
- $k_{-1}$: Recombination rate constant
- $k_B$: Boltzmann constant
- $\ell$: Bjeruum length
- $n$: Outward normal unit vector
- $n_{ij}$: Microscopic concentration of ions of type $j$ near an ion of type $i$
- $n_m$: Macroscopic concentration of species $m$
- $N_m$: Flux of species $m$
- $S_m$: Surface area of a face of a 6-dimensional cube
- $t$: Time
- $T$: Absolute temperature
- $U_{ij}$: Potential energy of an ion of type $j$ near an ion of type $i$
- $v_{ij}$: Velocity of ions of type $j$ near an ion of type $i$
- $V_1$: Volume of a differential volume element
- $z_i$: Number of elementary charges carried by an ion of type $i$
- $\alpha$: Dimensionless closest distance of approach
- $\gamma$: Dimensionless ration of the Bjerrum length to the Debye length
- $\varepsilon$: Dielectric permittivity
- $\zeta$: Dimensionless position
- $\theta$: Geometry factor
- $\theta_g$: Dimensionless ration of the number of elementary charges
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\lambda$</td>
<td>Debye length</td>
</tr>
<tr>
<td>$\xi_1$</td>
<td>Position coordinate in 6-dimensional space</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Inverse of the dimensionless position</td>
</tr>
<tr>
<td>$\phi_j$</td>
<td>Dimensionless electrostatic potential near an ion of type $j$</td>
</tr>
<tr>
<td>$\Phi_i$</td>
<td>Electrostatic potential near an ion of type $i$</td>
</tr>
</tbody>
</table>
Chapter 2: Dissociation of Weak Electrolytes in the Presence of an Electric Field

Abstract

The dissociation of weak electrolytes is increased by an applied electric field. Lars Onsager's classic treatment of this increase in dissociation determines the effect of an applied electric field upon the movement of a pair of ions formed by dissociation.\textsuperscript{1,2} To obtain an analytic expression, Onsager approximates that the pair of ions form a chemical bond when they are at a separation distance of zero. This approximation is poor when long chemical bonds are involved, such as the dissociation of an electrolyte occurring via charge transport along a hydrogen-bond wire.

Here, the work of Onsager is extended to the case of dissociation via long chemical bonds. For bond lengths greater than zero, the results predict the recombination rate constant of a collision-controlled reaction will increase with an applied electric field. Additionally, results predict that the dissociation of a weak electrolyte will increase with an applied electric field. The increase in dissociation is predicted to vary by orders of magnitude with small changes in the length of the chemical bond.

Introduction

When aqueous weak electrolytes are exposed to large electric fields, three important phenomena occur. The first effect is an increase in the dissociation of the weak electrolyte. This effect will take place at electric fields as small as tens of kilovolts per centimeter.\textsuperscript{3} The second effect is dielectric breakdown. When an aqueous electrolyte undergoes dielectric breakdown, electrons begin to carry current through the solution. Dielectric breakdown is seen to occur in distilled water at electric fields of 650 to 700 kilovolts per centimeter.\textsuperscript{4} The third effect is dielectric saturation. When dielectric saturation occurs, the molecular dipoles in a material begin to align. Dielectric saturation is predicted to occur in water at electric fields in excess of 1000 kilovolts per centimeter.\textsuperscript{5}

Very large electric fields, on the order of ten thousand kilovolts per centimeter, are predicted to exist at interfaces in electrochemical systems.\textsuperscript{6} We are interested in how this large of an electric field will impact the dissociation of a weak electrolyte. In the bulk of a weak-electrolyte solution, this large of an electric field would lead to dielectric breakdown. However, when the electric field occurs only at an interface, it does not lead to dielectric breakdown. The work done here investigates the increase in dissociation of weak electrolytes with electric fields as large as thousands of kilovolts per centimeter.

Early experimental investigations of the increase in the dissociation of weak electrolytes with an applied electric field were conducted by Max Wien.\textsuperscript{7} It was found that under the influence of large electric fields, on the order of tens of kilovolts per centimeter, the conductivity of an electrolyte increased. A small increase in conductivity, of about 2%, was observed in strong 1-1 electrolytes. The effect, later called the First Wien Effect, was attributed to the large electric field eliminating the Debye-Hückel ionic atmosphere.\textsuperscript{3} When weak electrolytes were subjected to a large electric field, a similar but larger increase in the conductivity was observed. Under the influence of electric fields of tens of kilovolts per centimeter, an increase in conductivity of about 10% was observed.\textsuperscript{3} This increase, later called the Second Wien Effect, was attributed to increased dissociation of the weak electrolyte.
Conceptually, one can attribute increased dissociation to two different effects. The first effect is that, when a weak-electrolyte molecule undergoes dissociation, there is an intermediate state where the charges are separated over the length of the chemical bond. When the electric field is applied, this state of charge separation will be favored, and the degree of dissociation will increase. The second effect is that, after a weak-electrolyte molecule undergoes dissociation, the resulting ions diffuse apart. As the ions diffuse, they are electrostatically attracted to each other and often recombine. Under the influence of an applied electric field, this electrostatic attraction becomes less significant compared to the applied electric field.

The classic theory of the Second Wien Effect was published by Lars Onsager in 1934.\(^1\) Onsager approximates the dissociation of a weak electrolyte as a series of steps: molecules ⇄ pairs ⇄ ions. He treats the second step, pairs ⇄ ions, using statistical mechanics. The movement of the ions is described using the Nernst-Planck equation. This movement of the ions is influenced by the applied electric field as well as the coulombic attraction between the pairs of ions. The approach neglects any influence of a Debye-Hückel ionic atmosphere.

Onsager's theory does not account for any change in the equilibrium of the step molecules ⇄ pairs due to the applied electric field. Onsager does not account for a change in the equilibrium of this step because to obtain an analytic expression for the pairs ⇄ ions problem, he was forced to approximate the pairs as existing at a distance of zero separation. In actuality, the pairs will have a small yet finite separation. Therefore, the applied electric field will favor the separation of charges. Onsager analyzes his approximation and concludes that as long as the Coulomb field dominates the applied electric field at the distance of charge separation in the pairs, then the approximation is valid.

Conversely, neglecting the change in the equilibrium of the step pairs ⇄ molecules is a poor approximation when the Coulomb field between the two ions does not dominate over the applied electric field. This situation will occur when there are large electric fields and large distances of separation of the charges in the pairs.

The distance of separation of the charges in the pairs is predicted to be large in the case of weak-electrolyte dissociation involving charge transfer over a hydrogen-bond wire.\(^8,9,10\) Under these conditions, the length of the hydrogen-bond wire can be around 0.6 nm. At this distance, the contribution to the electric field due to the Coulomb field between the two ions is about five hundred kilovolts per centimeter. Since the electric field at an interface is larger than the coulomb field between the charges in the pairs, Onsager’s approximation is poor for dissociations involving charge transfer along a hydrogen-bond wire occurring at an electrochemical interface.

The results are calculated in this work as a function of the applied electric field and the length of the chemical bond. The recombination rate constant of the ions → pairs step is determined for collision-controlled reactions. The change in the dissociation rate constant of the overall reaction, molecules → pairs → ions, is calculated. Additionally, since the recombination rate constant and the change in the dissociation rate constant are calculated, the change in the dissociation equilibrium constant is known.

This work is similar to the previous treatment by Onsager in that the movement of the ions is accounted for as a function of the applied electric field. However, different from Onsager’s treatment, the ions are not assumed to be at zero distance of charge separation.
when the dissociation occurs. Rather, the ions are assumed to be distributed following a Boltzmann distribution on the surface of a sphere with a radius corresponding to the length of the chemical bond. This work is then an extension of Onsager’s work in both the treatment of the molecules ⇋ pairs step and the pairs ⇋ ions step. The equations are solved numerically. Results are reported for a number of different bond lengths. The dissociation of water is used as an example.

Molecular Model of Dissociation

The dissociation of a weak-electrolyte molecule in an aqueous solution is described by treating the weak electrolyte as six different species. The first species is an undissociated weak electrolyte in an orientation such that it will not undergo dissociation. This species will be denoted by \((AB)\). The second species is an undissociated weak electrolyte in which it and the surrounding solvent molecules are orientated such that dissociation can occur. This species is denoted by \((AB)^{‡}\). The third species is an undissociated weak electrolyte along which charge has separated, forming a dipole with a distance of \(a\) between the charges. This species is denoted by \(A^{+} \cdots B^{-}\). The fourth species is an ion pair at a separation of \(a\), denoted by \(A_{a}^{+}B_{a}^{-}\). Finally, the fifth and sixth species are free ions in solution a substantial distance apart and are denoted by \(A^{+}\) and \(B^{-}\). These free ions are the only species that contribute to the conductivity of the solution.

The dissociation and recombination of a weak electrolyte can be written so that it follows the scheme

\[
\begin{align*}
(AB) & \rightleftharpoons (AB)^{‡} \rightleftharpoons A^{+} \cdots B^{-} \rightleftharpoons A_{a}^{+}B_{a}^{-} \rightleftharpoons A^{+} + B^{-}.
\end{align*}
\]

(2.1)

The rate constants associated with the forward reactions are given by \(k_{\alpha}\), \(k_{\beta}\), \(k_{\gamma}\), and \(k_{\delta}\). The rate constants associated with the reverse reactions are given by \(k_{-\alpha}\), \(k_{-\beta}\), \(k_{-\gamma}\), and \(k_{-\delta}\).

The dissociation reaction that is of most interest in this thesis is the dissociation of water into hydronium ions and hydroxide ions. The dissociation of water is treated as conforming to a scheme as presented in Equation 2.1. The scheme given by Equation 2.1 for the dissociation of a general weak electrolyte is displayed in Figure 2.1 for the case of water dissociation.
The dissociation of a water molecule following the scheme proposed in Equation 2.1. The different configurations in the figure correspond to the species as: configuration I to (AB), configuration II to (AB)^+, configuration III to A^+ ⋯ B^−, configuration IV to A_a^+B_a^−, and configuration V to A^+ and B^−.

The scheme for water dissociation given by Equation 2.1 and displayed in Figure 2.1 is simplified from the molecular-dynamics results of Geissler et al. These molecular-dynamics results show that, in the absence of a macroscopic electric field, the dissociation of water
involves the collective alignment of the surrounding water molecules such that they produce an electric field to drive the dissociation of a water molecule. The dissociation of a water molecule is seen to occur over a chain of hydrogen bonds between a few water molecules. Geissler et al. put the number of water molecules in the chain at a minimum of four as is displayed in Figure 2.1. Geissler et al. point out that the length of this chain is ~0.6 nm. This distance of 0.6 nm is also the recombination distance for the experimental recombination of hydronium and hydroxide ions.8,9

**Equilibrated Steps in the Reaction Scheme**

We are interested in describing the recombination and dissociation rate constants of a weak electrolyte as a function of the applied electric field. We are interested in the case of a collision-controlled reaction. Since the reaction is collision controlled, the reactions in steps $\alpha$, $\beta$, and $\gamma$ are in equilibrium, and follow a Boltzmann distribution. However, the rate of step $\delta$ in Equation 2.1 does not follow a Boltzmann distribution when the electric field is applied. Rather, the movement of ions in step $\delta$ follows the Nernst-Planck equation.

Since steps $\alpha$, $\beta$, and $\gamma$ are in a state of true equilibrium, the concentrations of species $(AB)$, $(AB)^\dagger$, $A^+ \cdots B^-$, and $A_\alpha^+ B_\alpha^-$ follow a Boltzmann distribution. The ratios of the four species are then given by

$$ \frac{n_{(AB)^\dagger}}{n_{(AB)}} = \frac{k_\alpha}{k^-_{\alpha}} = \frac{g_{(AB)^\dagger}}{g_{(AB)}} \exp \left( \frac{-U_{(AB)^\dagger}}{k_B T} \right), $$

(2.2)

$$ \frac{n_{A^+ \cdots B^-}}{n_{(AB)^\dagger}} = \frac{k_\beta}{k^-_{\beta}} = \frac{g_{A^+ \cdots B^-}}{g_{(AB)^\dagger}} \exp \left( \frac{-U_{A^+ \cdots B^-}}{k_B T} \right), $$

(2.3)

and

$$ \frac{n_{A_\alpha^+ B_\alpha^-}}{n_{A^+ \cdots B^-}} = \frac{k_\gamma}{k^-_{\gamma}} = \frac{g_{A_\alpha^+ B_\alpha^-}}{g_{A^+ \cdots B^-}} \exp \left( \frac{-U_{A_\alpha^+ B_\alpha^-}}{k_B T} \right), $$

(2.4)

In Equations 2.2 through 2.4, $n_x$ is the concentration of species $x$, $g_x$ is the degeneracy of species $x$, and $U_x$ is the potential energy associated with species $x$. Combining Equations 2.2 through 2.4 yields

$$ \frac{n_{A_\alpha^+ B_\alpha^-}}{n_{(AB)}} = \frac{g_{A_\alpha^+ B_\alpha^-}}{g_{(AB)}} \exp \left( \frac{-U_{A_\alpha^+ B_\alpha^-}}{k_B T} \right). $$

(2.5)

The potential energies $U_{(AB)}$ and $U_{A_\alpha^+ B_\alpha^-}$ depend on the local electric field experienced by the molecules. The potential energy of the molecules changes in the electric field due to polarization of the electron densities and the alignment of permanent dipoles. The molecular polarization and dipole alignment have been used to predict the dielectric permittivity of liquids with some success.11 In addition to molecular polarization and dipole alignment, the potential
energy \( U_{\text{A}^+\text{B}^-} \) includes a contribution due to charges being separated by a distance of \( a \) in the electric field.

It is assumed that the potential energy of molecules in an electric field can be described as a sum of contributions due to molecular polarization and alignment of permanent dipoles. When the molecules are in a macroscopic electric field of \( E \), the potential energy \( U_{\text{AB}} \) is given by

\[
U_{\text{AB}} = U_{\text{AB}}^0 + U_{\text{AB}}^{\text{polarization}} + U_{\text{AB}}^{\text{dipole}}.
\]  

(2.6)

In Equation 2.6, \( U_{\text{AB}}^0 \) is the potential energy in the absence of a local electric field, \( U_{\text{AB}}^{\text{polarization}} \) is the change in potential energy due to molecular polarization, and \( U_{\text{AB}}^{\text{dipole}} \) is the change in potential energy due to alignment of permanent dipoles. The potential energy \( U_{\text{A}^+\text{B}^-} \) is given by

\[
U_{\text{A}^+\text{B}^-} = U_{\text{A}^+\text{B}^-}^0 + U_{\text{A}^+\text{B}^-}^{\text{polarization}} + U_{\text{A}^+\text{B}^-}^{\text{dipole}} - eEa\cos(\theta).
\]  

(2.7)

In Equation 2.7, \( U_{\text{A}^+\text{B}^-}^0 \) is the potential energy in the absence of a local electric field, \( U_{\text{A}^+\text{B}^-}^{\text{polarization}} \) is the change in potential energy due to molecular polarization, \( U_{\text{A}^+\text{B}^-}^{\text{dipole}} \) is the change in potential energy due to the alignment of permanent dipoles, \( e \) is the elementary charge, \( E \) is the magnitude of the macroscopic electric field, and \( \theta \) is the angle between the macroscopic electric field and a vector pointing from the negative charge to the positive charge.

The potential energy of the various species could be determined from measurement or from simulation. In the absence of performing additional measurements or calculations it is assumed that

\[
U_{\text{AB}}^{\text{polarization}} = U_{\text{A}^+\text{B}^-}^{\text{polarization}},
\]  

(2.8)

and

\[
U_{\text{AB}}^{\text{dipole}} = U_{\text{A}^+\text{B}^-}^{\text{dipole}}.
\]  

(2.9)

The assumption of Equation 2.8 physically means that the effect of the macroscopic electric field upon the polarization of species \( \text{A}^+\text{B}^- \) is the same as the effect of the macroscopic electric field upon the polarization of species \( \text{AB} \). Assumption of Equation 2.9 physically means that the effect of the macroscopic electric field upon the alignment of dipoles in species \( \text{A}^+\text{B}^- \) is the same as the effect of the macroscopic electric field upon the alignment of dipoles in species \( \text{AB} \). This approximation is chosen because it simplifies the resulting expressions and does not introduce additional unknown parameters. It is also assumed that the degeneracy of the species is unchanged by the macroscopic electric field.

When the applied electric field is zero, the ratio of the concentrations is

\[
\frac{n_{\text{A}^+\text{B}^-}^0}{n_{\text{AB}}^0} = \frac{g_{\text{A}^+\text{B}^-} \exp\left( -\frac{U_{\text{A}^+\text{B}^-}^0}{k_BT} \right)}{g_{\text{AB}} \exp\left( -\frac{U_{\text{AB}}^0}{k_BT} \right)}.
\]  

(2.10)

In Equation 2.10, the superscript 0 indicates that the applied electric field is zero. Using statistical mechanics, the presence of a local electric field can be taken into account so that
\[
\frac{n_{A^+B^-}}{n_{(AB)}} = \frac{n_{A^+B^-}^0}{n_{(AB)}^0} \exp \left(\frac{eEa \cos(\theta)}{k_B T}\right),
\]  
Equation 2.11

The ratio of concentrations can be replaced by an equilibrium constant such that

\[
K_{\alpha-\gamma}^0 = \frac{n_{A^+B^-}^0}{n_{(AB)}^0}.
\]  
Equation 2.12

Equation 2.11 then becomes

\[
\frac{n_{A^+B^-}}{n_{(AB)}} = K_{\alpha-\gamma}^0 \exp \left(\frac{eEa \cos(\theta)}{k_B T}\right).
\]  
Equation 2.13

Note that \(K_{\alpha-\gamma}^0\) is the equilibrium constant relating the equilibrium concentrations of the species involved in steps \(\alpha\) thru \(\gamma\) for the dissociation reaction given by Equation 2.1. The equilibrium constant \(K_{\alpha-\gamma}^0\) is not the overall dissociation constant for the dissociation reaction given in Equation 2.1. The overall dissociation constant must include step \(\delta\) as well. Step \(\delta\) will be included by solving for the distribution of ions near a central ion under the influence of the applied electric field. Equation 2.13 will later be used to determine the boundary condition for the distribution of ions.

Governing Equations for the Enhanced Separation of Ions Due to an Applied Electric Field

When a weak electrolyte is subjected to a large electric field, the degree of dissociation tends to increase. This is known as the second Wien effect. Onsager first treated this effect by considering the impact of the applied electric field upon the movement of the ions apart from each other.\(^5\) To do this, Onsager used the same distribution-function approach as used in Chapter 1 to calculate the rate of recombination of ions. As the ions move apart, three different driving forces need to be considered: concentration gradients, the electrostatic attraction of the ions, and the force on the ions due to the applied electric field. Equation 2.13 will later be used to determine the boundary condition for the distribution of ions.

For the potential energies, Onsager uses the assumption of Debye and Hückel, expressed as

\[
U_{ji} = z_i e \Phi_j
\]  
Equation 2.14

and

\[
U_{ij} = z_j e \Phi_i.
\]  
Equation 2.15

Equations 2.14 and 2.15 are similar to Equation 1.110; however the 0 superscripts have been removed to indicate that the system is not necessarily at equilibrium. Additionally, it is no longer true that \(U_{ij} = U_{ji}\). This is because if the ions have different charges, the external field influences an ion of type \(i\) differently from an ion of type \(j\). The electrostatic potentials in Equations 2.14 and 2.15 are a combination of the potential due to the electrostatic attraction of the two ions and the applied electric field.

Following Onsager, we make the assumption that the electrostatic attraction of the two ions is well approximated by a Coulomb potential. This assumption neglects the presence of an ion cloud. The assumption is valid when calculating the distribution of ions for distances of separation much less than the Debye length. The expressions for the electrostatic potential are then

\[
\Phi_j(r_1, r_2) = -\frac{k_B T}{z_i e} \left[\frac{2\ell}{|r_2 - r_1|} - \frac{E \cdot r_2}{|r_2 - r_1|}\right]
\]  
Equation 2.16

\(\ell\) is the Debye length and \(E\) is the applied electric field.
and

\[ \Phi_i(r_1, r_2) = -\frac{k_B T}{z_i e} \left( \frac{2\ell}{|r_2 - r_1|} - E \cdot r_2 \right). \]  

(2.17)

Here \( \Phi_i \) is the electrostatic potential at \( r_2 \) when there is an ion of type \( i \) at \( r_1 \). Similarly, \( \Phi_j \) is the electrostatic potential at \( r_1 \) when there is an ion of type \( j \) at \( r_2 \). The \( \ell \) represents the Bjerrum length as defined by Equation 1.47. Combining the expressions for the electrostatic potentials, Equations 2.16 and 2.17, with the expressions for the potential energies, Equations 2.14 and 2.15, yields

\[ U_{ji} = -k_B T \left( \frac{2\ell}{|r_2 - r_1|} - z_i e E \cdot r_2 \right). \]  

(2.18)

and

\[ U_{ij} = -k_B T \left( \frac{2\ell}{|r_2 - r_1|} - z_j e E \cdot r_1 \right). \]  

(2.19)

The ions are expected to move following a Nernst-Planck expression. The relevant equations are Equation 1.19 and Equation 1.20. Using the potential energies given by Equation 2.18 and Equation 2.19, the Nernst-Planck expressions become

\[ v_{ji} = -\frac{D_i}{k_B T} \left( -k_B T \nabla_2 \left( \frac{2\ell}{|r_2 - r_1|} - z_i e + k_B T \nabla_2 \ln f_{ji} \right) \right) \]  

(2.20)

and

\[ v_{jj} = -\frac{D_j}{k_B T} \left( -k_B T \nabla_1 \left( \frac{2\ell}{|r_2 - r_1|} - z_j e + k_B T \nabla_1 \ln f_{ij} \right) \right). \]  

(2.21)

By introducing \( \nu \), where \( \nu = r_2 - r_1 \), and making use of Equations 1.22 and 1.23, the velocity difference can be written as

\[ v_{ji} - v_{jj} = (D_i + D_j) \nabla \ln f_{ji} - (D_i + D_j) \nabla \left( \frac{2\ell}{\nu} \right) - (z_i D_i - z_j D_j) \frac{e E}{k_B T}. \]  

(2.22)

In Equation 2.22, the terms on the right are firstly due to concentration gradients, secondly due to the electrostatic attraction of the ions, and thirdly due to the applied electric field.

Combining the velocity difference, Equation 2.22, with the continuity equation, Equation 1.16, yields

\[ \frac{\partial f_{ji}}{\partial t} = (D_i + D_j) \left( \nabla^2 f_{ji} - \nabla f_{ji} \cdot \nabla \left( \frac{2\ell}{\nu} \right) - (z_i D_i - z_j D_j) \frac{e E}{k_B T} \nabla f_{ji} \cdot E \right). \]  

(2.23)

Equation 2.27 is the equation that will be solved to determine the rate at which ions diffuse apart in an applied electric field.

The coordinate system for the applied electric field is chosen such that the applied electric field is oriented along the z-axis in the positive direction. The electric field is then given by

\[ E = E e_z. \]  

(2.24)

In Equation 2.24, \( E \) is the magnitude of the applied electric field and is always positive. The continuity equation is then

\[ \frac{\partial f_{ji}}{\partial t} = (D_i + D_j) \left( \nabla^2 f_{ji} - \nabla f_{ji} \cdot \nabla \left( \frac{2\ell}{\nu} - z_i D_i - z_j D_j \frac{e E z}{D_i + D_j k_B T} \right) \right). \]  

(2.25)
Additionally, the charges on the two ions, \( z_i \) and \( z_j \), are of opposite sign. They are arbitrarily chosen such that

\[ z_j > 0, \]  

and

\[ z_i < 0. \]  

Then the group of variables involving the applied electric field always satisfy the inequality

\[ \frac{z_i D_i - z_j D_j}{D_i + D_j} \frac{eE}{k_B T} \geq 0. \]  

This leads to the introduction of the parameter \( \beta \), defined as

\[ 2\beta = \left| \frac{z_i D_i - z_j D_j}{D_i + D_j} \frac{eE}{k_B T} \right|. \]  

This parameter has dimensions of inverse length. The parameter is essentially a measure of the strength of the applied electric field on the movement of the ions apart from one another. In the simplest case \( z_j = +1 \) and \( z_i = -1 \). Equation 2.29 then reduces to

\[ 2\beta = \left| \frac{eE}{k_B T} \right|. \]  

In Equation 2.30, it is easy to see that \( \beta \) is directly related to the strength of the electric field.

The \( \beta \) parameter can be used to write the continuity equation as

\[ \frac{\partial f_{ji}}{\partial t} = (D_i + D_j) \left( \nabla^2 f_{ji} - \nabla f_{ji} \cdot \nabla \left( \frac{2\ell}{r} + 2\beta z \right) \right). \]  

This is the continuity equation that is solved in the following sections to determine the rate at which the ions move apart during dissociation. The term involving \( \beta \) accounts for the applied electric field.

In the event that the opposite arbitrary choices were made for 2.26 and 2.27, then the opposite equality would hold in Equation 2.28. This would lead to a continuity equation as

\[ \frac{\partial f_{ji}}{\partial t} = (D_i + D_j) \left( \nabla^2 f_{ji} - \nabla f_{ji} \cdot \nabla \left( \frac{2\ell}{r} - 2\beta z \right) \right). \]  

Proceeding with Equation 2.32 rather than 2.31 leads to identical results.

At steady state, Equation 2.31 reduces to

\[ \nabla^2 f_{ji} = \nabla f_{ji} \cdot \nabla \left( \frac{2\ell}{r} + 2\beta z \right). \]  

This is the governing equation that is solved to determine the rate at which the ions are separating. Equation 2.33 was first published by Onsager in 1934.\(^1\) It is important to point out that Equation 2.33 is linear in \( f_{ji} \). Equation 2.33 linear in \( f_{ji} \) because a Columbic potential was used rather than a potential obtained by solving Poisson’s equation.

Just as in Chapter 1, the solution of the continuity equation can be related to the rate of dissociation using the divergence theorem. Using the divergence theorem, Equation 2.31 becomes

\[ \int \frac{\partial f_{ji}}{\partial t} dV = \oint (D_i + D_j) \left( \nabla f_{ji} - f_{ji} \nabla \left( \frac{2\ell}{r} + 2\beta z \right) \right) \cdot n dS. \]  

The right side of Equation 2.34 is the flux of ions into a surface. We will apply Equation 2.34 on a spherical surface at \( r = a \). This spherical surface represents where the chemical bond is
formed. Outside of this sphere, the distribution function is at steady state and follows Equation 2.33. Inside of the sphere, the generation or consumption of ions takes place. Equation 2.34 then relates the rate at which the ions are crossing the spherical surface at \( r = a \) to the rate that the ions are generated or consumed within the sphere. The rate of generation or consumption is the rate of recombination or dissociation of ions in solution. By solving Equation 2.33 with appropriate boundary conditions, the distribution function of ions can be determined. Using the distribution function, Equation 2.34 can be solved to yield the rate of dissociation or recombination.

Additionally, one can write a flux equation for the ions in terms of the distribution function. We can introduce \( N \) as the flux of the ions such that

\[
N = f_{ji} (v_{ji} - v_{ij}).
\]  
(2.35)

The flux equation is then

\[
N = (D_i + D_j) \left( -\nabla f_{ji} + f_{ji} \nabla \left( \frac{2\ell}{r} + 2\beta z \right) \right).
\]  
(2.36)

In Equation 2.36, it can be seen that the flux of the ions is driven by a term due to diffusion and a term due to migration of ions in an electric field. By combining Equation 2.33 and Equation 2.36 we see that \( 0 = \nabla \cdot N \).

A major contribution to the literature contained in this chapter is a new choice of boundary conditions for Equation 2.33. Onsager's solution of Equation 2.33 assumes that the bond length at dissociation is zero. The choice of zero bond length allows for an analytic solution. In this chapter, Equation 2.33 is solved for nonzero bond lengths. The new boundary conditions are given in the next section. An outline of Onsager's solution is given later in this chapter in the section entitled Solution for Zero Bond Length.

**Boundary Conditions**

Solving Equation 2.33 will yield the distribution function. The rate of recombination or dissociation is determined by using the distribution function and Equation 2.34. We are interested in the distribution function for three different cases: recombination, dissociation, and equilibrium. The distribution function for each of these cases corresponds to a different set of boundary conditions. Since Equation 2.33 is linear, the solution to any case is a linear combination of the solutions to the other two cases.

In the case of recombination, the boundary conditions are

\[
f_{ji} \bigg|_{r=a} = 0
\]  
(2.37)

and

\[
f_{ji} \bigg|_{r=\infty} = n_i n_j.
\]  
(2.38)

In Equation 2.38, \( n_i n_j \) is a constant. Equation 2.37 and Equation 2.38 are the boundary conditions for the recombination case because they set a bulk value of the distribution function when the ions are far apart and a zero value of the distribution function when the ions are separated by the bond length. Thus the ions are diffusing together and reacting.

In the case of dissociation, the boundary conditions are

\[
f_{ji} \bigg|_{r=a} = n_i^0 n_j^0 \exp \left( \frac{2\ell}{a} + 2\beta a \cos(\theta) \right)
\]  
(2.39)

and
\[ f_{ji}\big|_{r=\infty} = 0. \]  

In Equation 2.39, \( n_i^0 n_j^0 \) is a constant. Equation 2.39 imposes a Boltzmann distribution of the distribution function at \( r = a \), which acts as a source of ions. Equation 2.40 acts as a sink of ions.

The sign of \( +2\beta a \cos(\theta) \) in Equation 2.39 should be noted. The sign is due to the choice of Equation 2.26, Equation 2.27, the convention that a positive electric field is being applied along the z-axis, and that \( \theta \) is the angle between the macroscopic electric field and a vector pointing from the negative charge to the positive charge.

In the case of equilibrium, the boundary conditions are Equation 2.38, Equation 2.39 and that

\[ 0 = \int_0^\pi N_r |r=a| \sin \theta \, d\theta. \]  

In Equation 2.41, \( N_r \) is the flux normal to the surface of the sphere. Equation 2.41 is found by setting Equation 2.34 equal to zero and applying it over the surface of the sphere. Equation 2.41 is physically interpreted as that the overall rate of dissociation and recombination are zero. The ratio of \( n_i n_j \) to \( n_i^0 n_j^0 \) is specified by Equation 2.41.

**Solution at Zero Electric Field**

It is instructive to consider the solution for each case when the macroscopic electric field is zero. When the macroscopic electric field is zero, Equation 2.33 becomes

\[ \frac{d}{dr} \left( r^2 \frac{df_{ji}}{dr} \right) = -2\ell \frac{df_{ji}}{dr}. \]  

For the case of recombination with an electric field of zero, Equation 2.42 is solved with boundary conditions given by Equation 2.37 and Equation 2.38. The solution is

\[ f_{ji} = n_i n_j \exp \left( \frac{2\ell}{r} \right) \left( 1 - \exp \left( \frac{2\ell}{a} \right) \right). \]  

Using Equation 2.34, with the distribution function given by Equation 2.43, one can solve for the recombination rate constant since

\[ k_{-\delta} = \frac{1}{n_i n_j} \int \frac{\partial f_{ji}}{\partial t} \, dV = 4\pi (D_i + D_j) a \frac{2\ell}{1 - \exp \left( -\frac{2\ell}{a} \right)}. \]  

Equation 2.44 is the same as Equation 1.175 in the limit of an infinite Debye length.

For the case of dissociation with an electric field of zero, Equation 2.42 is solved with boundary conditions given by Equation 2.39 and Equation 2.40. The solution is

\[ f_{ji} = n_i^0 n_j^0 \exp \left( \frac{2\ell}{a} \right) \left( 1 - \exp \left( \frac{2\ell}{r} \right) \right). \]  

Using Equation 2.34, with the distribution function given by Equation 2.45, one can solve for the dissociation rate constant since
\( k_\delta = -\frac{1}{n_{A^+}B^-} \int \frac{\partial f_{ji}}{\partial t} dV = 4\pi (D_i + D_j) a \frac{2\ell}{a} \frac{n_i^0 n_j^0}{1 - \exp \left( -\frac{2\ell}{a} \right) n_{A^+}B^-} \) \hspace{1cm} (2.46)

For the case of equilibrium with an electric field of zero, Equation 2.42 is solved with boundary conditions given by Equation 2.38 and Equation 2.39. The solution is

\[
f_{ji} = n_i^0 n_j^0 \left( 1 - \exp \left( \frac{2\ell}{r} \right) \right) + n_i n_j \frac{\exp \left( \frac{2\ell}{r} \right) - \exp \left( \frac{2\ell}{a} \right)}{1 - \exp \left( \frac{2\ell}{a} \right)} \]

\hspace{1cm} (2.47)

Notice that Equation 2.47 is the sum of Equation 2.43 and Equation 2.47. Applying Equation 2.41 it is found that

\[
n_i n_j = n_i^0 n_j^0. \]

\hspace{1cm} (2.48)

Thus, Equation 2.47 reduces to

\[
f_{ji} = n_i n_j \exp \left( \frac{2\ell}{r} \right). \]

\hspace{1cm} (2.49)

As expected, Equation 2.49 is a Boltzmann distribution. The distribution functions for the case of recombination, dissociation, and equilibrium; given by Equation 2.43, Equation 2.45, and Equation 2.49, respectively; are shown in Figure 2.2.

![Figure 2.2](image)

**Figure 2.2.** The distribution functions for the case of zero macroscopic electric field. The results shown are for the case of \( a = 0.58 \) nm and \( \ell = 0.358 \) nm. These are the parameters that occur in liquid water at STP.

**Solution for Bond Length of Zero**

Lars Onsager was able to obtain an analytical solution to Equation 2.33 with a macroscopic electric field in the limit that the bond length between the dissociating ions is zero.
Later in this chapter, Onsager’s work will be extended to bond lengths of greater than zero by solving Equation 2.33 numerically. This section is what I have summarized from Onsager’s publications on the solution for a bond length of zero. Onsager outlined his solution method in 1934 and 1935.\textsuperscript{1,2}

In short, what Onsager does is break the problem up into two pieces: the distribution function during recombination, and the distribution function during dissociation. Since the governing equation is linear, the combination of these two solutions is also a solution, namely the equilibrium solution. Onsager’s solution for the distribution function during recombination is fairly simple. Unfortunately, Onsager’s solution for the distribution function during dissociation “involves elaborate analysis.”\textsuperscript{1} Some of the details are explained below.

For the case of recombination with a macroscopic electric field, it is instructive to revisit the case of recombination in the absence of a macroscopic electric field. In this case we found that the distribution function is given by Equation 2.43. Values of Equation 2.43 are plotted in Figure 2.3 for various bond lengths.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{The distribution function given by Equation 2.43. The values on the plot are the values of $a/2\ell$.}
\end{figure}

As can be seen in Figure 2.3, in the limit that $a \to 0$ the distribution function becomes more uniform. However, the distribution is never completely uniform as it always must satisfy the boundary condition given by Equation 2.37. This leads to a singular problem as $a \to 0$. The outer solution to the distribution function is

\[ f_{ji} = n_j n_i. \] (2.50)
This is a uniform distribution. The inner solution to the distribution is not of interest because in the limit that \( a \to 0 \), the inner region becomes smaller and smaller and becomes irrelevant.

The distribution given by Equation 2.50 is not only the distribution function when \( \beta = 0 \), but is also the distribution when \( \beta > 0 \). This is because if a uniform electric field is applied to a uniform distribution, the resulting distribution will still be uniform. Therefore, Equation 2.50 is the distribution function during recombination in the limit that \( a \to 0 \) for any value of \( \beta \).

The recombination rate constant in the limit that \( a \to 0 \) for any value of \( \beta \) is then
\[
k_{-\delta} = 8\pi(D_i + D_j)\ell.
\]
Equation 2.51 can be found by taking the limit of \( a \to 0 \) of Equation 2.44. Equation 2.51 is the same as the expression for the recombination rate constant given previously as Equation 1.177, first attributed to Langevin.\(^{12}\)

In the event that \( a > 0 \), Equation 2.51 will not hold. Rather, the recombination rate constant will vary with the value of \( \beta \). This is because the distribution for \( a > 0 \) is not uniform, and as can be seen in Figure 2.3 for the case \( \beta = 0 \). The recombination rate constant for the case \( a > 0 \) was not treated by Onsager, but will be treated later in this chapter by numerical methods.

For the case of dissociation, Onsager solves Equation 2.33 with similar boundary conditions to Equation 2.39, Equation 2.40, and Equation 2.41. Onsager uses that \( f_{ji} \to 0 \) as \( r \to \infty \) and that the generation of \( f_{ji} \) at \( r = 0 \) matches the consumption of \( f_{ji} \) at \( r = 0 \) for the case of recombination.

Solving for the distribution function during dissociation when \( \beta > 0 \) is much more difficult than in the case of recombination. In the case of dissociation, the distribution is not uniform, and thus the applied electric field deforms the distribution. The analytic solution for dissociation with \( \beta > 0 \) can be found in Onsager’s thesis.\(^2\) This solution makes use of the separation of variables technique. This solution method will be used later in this chapter for the manipulation of Equation 2.37 into equations that are solved numerically for the case of \( a > 0 \). The solution that Onsager obtains contains an integral that he is unable to evaluate exactly.

Using an order-of-magnitude analysis, Onsager is able to evaluate the integral approximately. The distribution function is then combined with the material balance, Equation 2.34, to obtain
\[
k_{\delta} = 8\pi(D_i + D_j)\ell \frac{n_i^0 n_j^0}{n_{A^+_a B^-_a}^0} J_1 \left( \frac{4\sqrt{-\beta \ell}}{2\sqrt{-\beta \ell}} \right).
\]
In Equation 2.52, \( J_1 \) is the ordinary Bessel function of order 1. The quantities with a superscript 0 are the values with zero applied electric field. Onsager has assumed that the concentration of \( A^+_a B^-_a \) is not a function of the applied electric field.

Onsager’s solution for the dissociation equilibrium constant can then be found from the recombination and dissociation rate constants. Onsager arrives at
\[
K = \frac{k_{-\delta}}{k_{-\delta}} = K^0 \frac{J_1 \left( \frac{4\sqrt{-\beta \ell}}{2\sqrt{-\beta \ell}} \right)}{2\sqrt{-\beta \ell}}.
\]
In Equation 2.53, \( K \) denotes the dissociation constant for the weak electrolyte. The value of \( K^0 \) is given by
\[
K^0 = \frac{n_i^0 n_j^0}{n_{A^+_a B^-_a}^0}.
\]
The expression can be expanded in a Taylor series around $\beta = 0$. The expansion yields

$$\frac{K}{K^0} = \sum_{m=0}^{\infty} \frac{1}{m! (m+1)!} (2b)^m.$$  \hspace{1cm} (2.55)

In Equation 2.55 $b$ is the dimensionless electric field defined as $b = 2\beta \ell$. A plot of Equation 2.55 is given in Figure 2.4.

![Graph showing $K/K^0$ vs. $b$](image)

**Figure 2.4.** The dissociation constant is seen to increase as the parameter $b$ increases. The parameter $b$ is a measure of the strength of the electric field compared to the strength of the attraction of the two ions.

**Critique of Onsager's Solution**

Onsager's solution method is impressive due to his ability to solve Equation 2.33 without the use of numerical methods. However, in order to obtain a solution, Onsager used a bond length of zero. In his thesis, Onsager comments on this use of zero length as a boundary condition. He gives two examples of plausible boundary conditions

$$N_r|_{r=a} = 0,$$  \hspace{1cm} (2.56)

and

$$f_{ij}|_{r=a} = \text{const.} \exp(2\beta a \cos \theta).$$  \hspace{1cm} (2.57)

Equation 2.56 is a no-flux boundary condition that corresponds to hard sphere ions with a distance of closest approach of $r = a$. Equation 2.56 is a Boltzmann distribution. The Boltzmann distribution corresponds to the boundary condition given by Equation 2.39. Onsager points out...
that in the limit of \( a \to 0 \), both of the boundary conditions given by Equations 2.56 and 2.57 become identical to the boundary condition used for Equation 2.53.

The validity of Onsager's solution is thus restricted to cases where \( a \approx 0 \). For boundary condition 2.57, this means that

\[
2\beta a \ll 1. \tag{2.58}
\]

For the case of water dissociation at 25°C, \( a = 5.8 \times 10^{-10} \) m, limiting the electric field to much less than \( 4.4 \times 10^7 \) V m\(^{-1}\). Data for weak electrolytes such as acetic acid in water have been measured to \( 2 \times 10^7 \) V m\(^{-1}\). We would therefore expect to start to see a deviation of Onsager's solution from the data at large applied electric fields.

Onsager states "in the majority of physical applications \( \exp \left( \frac{2\ell}{a} \right) \gg 1 \), and under this condition, the idealized problem (\( a = 0 \)) is a very good approximation to the actual state of affairs, provided that \( \beta \) is not too large."\(^{n1}\) For the dissociation of water at 25°C, \( \ell = 3.6 \times 10^{-10} \) m. Using the value of \( a = 5.8 \times 10^{-10} \) m leads to \( \exp \left( \frac{2\ell}{a} \right) = 3.44 \), which is greater, but not much greater than 1.

We are thus led to the conclusion that the approximation that \( a = 0 \) is not valid in the case of the dissociation of a weak electrolyte that occurs via a chain of hydrogen bonds, as occurs in water. The solution will be less valid at large electric fields. To obtain a valid solution, Equation 2.33 will be solved numerically with the boundary condition of 2.57. The solution will correspond to a greater increase of the dissociation constant of water due to the electric field than is predicted by Onsager's solution.

**Dimensionless Equations**

The problem of recombination and dissociation of weak electrolytes is solved numerically in this section. The numerical solution includes macroscopic electric fields and bond lengths greater than zero. The solution follows the separation of variables procedure used by Onsager.

To simplify the governing equations, they are recast in terms of dimensionless groups. The dimensionless length of the chemical bond is

\[
\alpha = \frac{a}{2\ell}. \tag{2.59}
\]

The dimensionless strength of the electric field is

\[
b = 2\ell\beta. \tag{2.60}
\]

The dimensionless radial position is

\[
R = \frac{r}{2\ell}. \tag{2.61}
\]

The dimensionless distribution function at infinity is

\[
f^\infty = \frac{n_in_j}{n_i^0n_j^0} = \frac{K}{K^0}. \tag{2.62}
\]

In Equation 2.62 the superscript 0 indicates the value at \( \beta = 0 \). The dimensionless distribution function is

\[
f = \frac{f_{ij}}{n_i^0n_j^0} - f^\infty. \tag{2.63}
\]
Equation 2.63 is chosen as the dimensionless distribution function so that \( f \) approaches zero as \( r \to \infty \) and to that \( f^\infty \) is easily interpreted in terms of the dissociation constant. The dimensionless flux is

\[
J = \frac{1}{D_i + D_j} \frac{2 \ell}{n_i^0 n_j^0} N
\]  

(2.64)

The angle from the z-axis is rewritten such that

\[
t = \cos \theta
\]  

(2.65)

The problem of interest is then to solve

\[
\nabla^2 f = \nabla f \cdot \nabla \left( \frac{1}{R} + 2bRt \right),
\]  

(2.66)

in the region

\[
0 \leq \alpha \leq R \leq \infty
\]  

(2.67)

and

\[
-1 \leq t \leq 1.
\]  

(2.68)

The boundary conditions for this problem depend upon the case of interest. For the case of recombination, the boundary conditions become

\[
f|_{R=\alpha} = -f^\infty
\]  

(2.69)

and

\[
f|_{R\to\infty} = 0.
\]  

(2.70)

For the case of dissociation, the boundary conditions become

\[
f|_{R=\alpha} = \exp \left( \frac{1}{\alpha} + 2b\alpha t \right) - f^\infty
\]  

(2.71)

and

\[
f|_{R\to\infty} = -f^\infty.
\]  

(2.72)

For the case of equilibrium, the boundary conditions are Equation 2.70 and Equation 2.71 and that

\[
0 = \int_{-1}^{1} J_{R}|_{R=\alpha} dt.
\]  

(2.73)

We are interested in solving Equation 2.66 with the various boundary conditions.

Separation of Variables

At this point, Equation 2.66 is not immediately separable. Following Onsager, we make the change of variables

\[
f = \varphi \exp \left( \frac{1}{2R} + bRt \right).
\]  

(2.74)

The governing equation is then

\[
\frac{\partial}{\partial R} \left( R^2 \frac{\partial \varphi}{\partial R} \right) + \frac{\partial}{\partial t} \left( (1 - t^2) \frac{\partial \varphi}{\partial t} \right) = \left( b^2 R^2 - bt + \frac{1}{4} R^{-2} \right) \varphi
\]  

(2.75)

The governing equation, Equation 2.75, is separable. Following the procedure of a separation-of-variables solution we write

\[
\varphi(R, t) = \sum_n c_n S_n(R) T_n(t).
\]  

(2.76)
In Equation 2.76, $c_n$ is a constant coefficient, $S_n(R)$ is a function of $R$ only and $T_n(t)$ is a function of $t$ only. Insertion into Equation 2.75 leads to two equations, one in the $R$ variable and one in the $t$ variable. The equation in the $t$ variable is

$$\frac{d}{dt} \left[ (1 - t^2) \frac{dT_n}{dt} \right] + (\mu_n + bt)T_n = 0. \tag{2.77}$$

The equation in the $R$ variable is

$$\frac{d}{dR} \left[ R^2 \frac{dS_n}{dR} \right] - \left( \mu_n + b^2 R^2 + \frac{1}{4} R^{-2} \right) S_n = 0. \tag{2.78}$$

In Equation 2.77 and Equation 2.78, $\mu_n$ is an eigenvalue. Equation 2.77 is a proper Strum-Liouville system. There is an infinite set of solutions for the eigenfunctions $T_n$ with the corresponding eigenvalues $\mu_n$. Since Equation 2.77 is a proper Strum-Liouville system, the functions $T_n$ and $T_m$ are orthogonal.

Solution in the $t$ Direction

In the limit that $\mu_n \gg bt$, Equation 2.77 becomes Legendre's differential equation. To take advantage of the properties of Legendre polynomials, deviation variables are introduced such that

$$T_n = P_n + W_n. \tag{2.79}$$

In Equation 2.79, $P_n$ represents the Legendre polynomial of order $n$, and $W_n$ is the remaining function. Additionally, the eigenvalues are written in terms of deviation variables as

$$\mu_n = n(n + 1) + \nu_n. \tag{2.80}$$

Expression 2.80 is used for the deviation variables because $n(n + 1)$ are the eigenvalues of Legendre's differential equation.

The governing equation in the $t$ coordinate then becomes

$$\frac{d}{dt} \left[ (1 - t^2) \frac{dW_n}{dt} \right] + (\nu_n + bt)P_n + (n(n + 1) + \nu_n + bt)W_n = 0. \tag{2.81}$$

The boundary conditions in the $t$ direction are

$$T_n|_{t=-1} = \text{finite}, \quad \tag{2.82}$$

and

$$T_n|_{t=1} = \text{finite}, \quad \tag{2.83}$$

and a normalization condition that

$$\int_{-1}^{1} T_n^2 dt = \frac{2}{n + \frac{1}{2}}. \quad \tag{2.84}$$

The first two conditions make sure that the function is remaining finite. The last condition is an arbitrary normalization condition. It is chosen so that $W_n$ is the same order of magnitude as $P_n$.

The boundary conditions used in the numerical solution must still be determined because $t = -1$ and $t = 1$ are singular points of the differential equation. To treat the singular point at $t = -1$ we introduce the parameter $\tau = 1 + t$. Rewriting Equation 2.77 in terms of $\tau$ yields

$$(2 - \tau) \frac{d^2 T_n}{d\tau^2} + 2(1 - \tau) \frac{dT_n}{d\tau} + (\mu_n + b(\tau - 1)) T_n = 0. \quad \tag{2.85}$$

A power series expansion of $T_n$ for small $\tau$ is
\[ T_n = \sum_{m=0} A_m \tau^m. \]  
(2.86)

In Equation 2.86, \( A_m \) is a constant. Inserting the power series expansion into Equation 2.85 yields

\[
(2 - \tau) \sum_{m=0} A_m m(m - 1) \tau^{m-1} + 2(1 - \tau) \sum_{m=0} A_m m \tau^{m-1} + \left( \mu_n + b(\tau - 1) \right) \sum_{m=0} A_m \tau^m = 0.
\]
(2.87)

Collecting terms in Equation 2.87 that are of order 0 in \( \tau \) yields

\[
2A_1 + (\mu_n - b)A_0 = 0.
\]
(2.88)

Using the relation given by Equation 2.88 and the power series expansion given by 2.86, in the limit that \( \tau \to 0 \) we have

\[
0 = \frac{dT_n}{d\tau} + \frac{1}{2} (\mu_n - b) T_n.
\]
(2.89)

Equation 2.89 becomes the boundary condition used at \( t = -1 \). Using the properties of Legendre polynomials, the boundary condition can be rewritten as

\[
0 = 2 \frac{dW_n}{dt} \bigg|_{t=-1} + n(n + 1) W_n \big|_{t=-1} + (\nu_n - b) \left( (-1)^n + W_n \big|_{t=-1} \right).
\]
(2.90)

Equation 2.90 replaces Equation 2.82 as the boundary condition at \( t = -1 \).

The singular point at \( t = 1 \) is treated in a similar manner. Thus, we introduce the parameter \( \omega = 1 - t \). Rewriting Equation 2.77 in terms of \( \omega \) yields

\[
(2 - \omega) \omega \frac{d^2 T_n}{d\omega^2} + 2(1 - \omega) \frac{dT_n}{d\omega} + \left( \mu_n + b(1 - \omega) \right) T_n = 0.
\]
(2.91)

A power series expansion of \( T_n \) for small \( \omega \) is

\[
T_n = \sum_{m=0} B_m \omega^m.
\]
(2.92)

In Equation 2.92, \( B_m \) is a constant. Inserting the power series expansion into Equation 2.91 yields

\[
(2 - \omega) \sum_{m=0} B_m m(m - 1) \omega^{m-1} + 2(1 - \omega) \sum_{m=0} A_m m \omega^{m-1} + \left( \mu_n + b(\omega - 1) \right) \sum_{m=0} A_m \omega^m = 0.
\]
(2.93)

Collecting terms in Equation 2.93 that are of order 0 in \( \omega \) yields

\[
2B_1 + (\mu_n - b)B_0 = 0.
\]
(2.94)

Using the relation given by Equation 2.94 and the power series expansion given by 2.92, in the limit that \( \omega \to 0 \) we have

\[
0 = \frac{dT_n}{d\omega} + \frac{1}{2} (\mu_n + b) T_n.
\]
(2.95)

Equation 2.95 is the boundary condition used at \( t = 1 \). Using the properties of Legendre polynomials, the boundary condition can be rewritten as

\[
0 = 2 \frac{dW_n}{dt} \bigg|_{t=1} - n(n + 1) W_n \big|_{t=1} - (\nu_n + b) \left( 1 + W_n \big|_{t=1} \right).
\]
(2.96)

Equation 2.96 replaces Equation 2.83 as the boundary condition at \( t = 1 \).
Using the properties of Legendre polynomials, the normalization condition given by Equation 2.84 can be rewritten as

$$\int_{-1}^{1} \left(2P_n W_n + W_n^2\right) dt = \frac{1}{n + \frac{1}{2}}.$$ (2.97)

The problem is then to solve Equation 2.81 subject to boundary conditions given by Equation 2.90 and Equation 2.97 and the normalization condition given by Equation 2.97. The boundary value problem is solved numerically using finite-difference techniques. The eigenvalue is treated as an additional unknown in the system. There is an infinite number of solutions to the problem. The eigenfunction and corresponding eigenvalue that is found is determined by the initial guess for $W_n$. The initial guess that is used is that $W_n \approx P_{n+1}$. The finite difference equations are programmed in Fortran and solved using BAND. Representative solutions are shown in Figure 2.5 for the cases of $b = 0.1$ and $b = 1.0$. The first four eigenvalues are given in Table 2.1.

![Figure 2.5](image)

**Figure 2.5.** The function $T_n$, the solution to Equation 2.77, is plotted as a function of $t$. On the left is the solution for $b = 0.1$. On the right is the solution for $b = 1.0$.

**Table 2.1.** The first four eigenvalues for the solution with $b = 0.1$ and $b = 1.0$.

<table>
<thead>
<tr>
<th>n</th>
<th>$b = 0.1$</th>
<th>$b = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_n$</td>
<td>$\mu_n$</td>
</tr>
<tr>
<td>0</td>
<td>$-1.666 \times 10^{-3}$</td>
<td>$-1.666 \times 10^{-3}$</td>
</tr>
<tr>
<td>1</td>
<td>$9.990 \times 10^{-4}$</td>
<td>2.001</td>
</tr>
<tr>
<td>2</td>
<td>$2.381 \times 10^{-4}$</td>
<td>6.000</td>
</tr>
<tr>
<td>3</td>
<td>$1.111 \times 10^{-4}$</td>
<td>12.000</td>
</tr>
</tbody>
</table>

**Solution in the R Direction**

The equation in the $R$ variable is given by Equation 2.78. To implement a numerical solution, the domain is transformed using $y = R^{-1}$. This is done so that the domain does not extend to infinity. The governing equation is then

$$\frac{d^2 S_n}{dy^2} - \left(\mu_n y^{-2} + b^2 y^{-4} + \frac{1}{4}\right) S_n = 0.$$ (2.98)

The domain then becomes
The boundary conditions are
\[ 0 \leq y \leq \alpha^{-1}. \tag{2.99} \]
\[ S_n|_{y=0} = 0 \tag{2.100} \]
and
\[ S_n|_{y=\alpha^{-1}} = 1. \tag{2.101} \]

The numerical problem is then to solve Equation 2.98 subject to boundary conditions given by Equation 2.100 and Equation 2.101. Representative solutions are shown in Figure 2.6 for the cases of \( b = 0.1 \) and \( b = 1.0 \) with \( \alpha = 0.810 \). This value of \( \alpha \) corresponds with a radius of 0.58 nm. This distance is chosen because it is the experimentally measured value for the distance of separation for the collision-controlled recombination of hydronium and hydroxide ions.  

![Figure 2.6](image)

**Figure 2.6.** The function \( S_n \), the solution to Equation 2.98, is plotted as a function of \( y \). On the left is the solution for \( b = 0.1 \). On the right is the solution for \( b = 1.0 \).

**Equilibrium Dissociation Constant**

It has now been shown how the functions \( T_n \) and \( S_n \) have been determined. Using the boundary conditions, given by Equations 2.69-2.73, the distribution functions for the cases of recombination, dissociation, and equilibrium can be constructed in terms of \( T_n \) and \( S_n \). The case of the equilibrium dissociation constant will be explored in the most depth. Later the recombination rate constant will be treated. The dissociation rate constant is simply the ratio of these two.

The equilibrium solution is constructed from the functions \( T_n \) and \( S_n \). Using the orthogonality of the functions \( T_n \), one can multiply both sides of Equation 2.76 by \( T_n \), integrate from \(-1\) to \( 1 \) in \( t \), and then evaluate the expression at \( y = \alpha^{-1} \) using the boundary condition Equation 2.71 to find that
\[
c_n = \frac{\int_{-1}^{1} T_n \left( \exp \left( \frac{1}{2\alpha} + bat \right) - f^\infty \exp \left( -\frac{1}{2\alpha} - bat \right) \right) \, dt}{\int_{-1}^{1} T_n^2 \, dt}. \tag{2.102} \]

Unfortunately, Equation 2.102 contains two variables that are not yet known: \( c_n \) and \( f^\infty \). The equation to determine \( f^\infty \) is the remaining unused boundary condition, Equation 2.73.

Rewriting Equation 2.73 in terms of \( y \) and \( \varphi \) yields
\[
0 = \int_{-1}^{1} \exp(\alpha bt) \frac{\partial \phi}{\partial y} \bigg|_{y=\frac{1}{\alpha}} \, dt \\
+ \exp \left( \frac{1}{2\alpha} \right) \left( \alpha \cosh(2\alpha b) - \frac{1}{2} \frac{1 + \alpha}{\alpha b} \sinh(2\alpha b) \right) \\
- f^\infty \exp \left( - \frac{1}{2\alpha} \right). 
\] (2.103)

With Equation 2.76, the derivative in Equation 2.103 can be expressed as
\[
\frac{\partial \phi}{\partial y} \bigg|_{y=\frac{1}{\alpha}} = \sum_n c_n \frac{\partial S_n}{\partial y} \bigg|_{y=\frac{1}{\alpha}} T_n. 
\] (2.104)

Equations 2.102, 2.103 and 2.104 can then be combined to yield
\[
f^\infty = \exp \left( \frac{1}{\alpha} \right) \frac{\sum_n A_n X_n - \frac{1}{2} \frac{1 + \alpha}{\alpha b} \sinh(2\alpha b) + \alpha \cosh(2\alpha b)}{1 + \sum_n B_n X_n}. 
\] (2.105)

And
\[
c_n = \exp \left( \frac{1}{2\alpha} \right) A_n - f^\infty \exp \left( - \frac{1}{2\alpha} \right) B_n. 
\] (2.106)

In Equations 2.105 and 2.106
\[
A_n = \frac{\int_{-1}^{1} T_n \exp(\alpha bt) \, dt}{\int_{-1}^{1} T_n^2 \, dt}, 
\] (2.107)
\[
B_n = \frac{\int_{-1}^{1} T_n \exp(-\alpha bt) \, dt}{\int_{-1}^{1} T_n^2 \, dt}, 
\] (2.108)

and
\[
X_n = \frac{\partial S_n}{\partial y} \bigg|_{y=\frac{1}{\alpha}} \int_{-1}^{1} T_n \exp(\alpha bt) \, dt. 
\] (2.109)

Equation 2.106 can then be used to determine each of the constants in Equation 2.76 and thus the distribution function. The parameter of interest in determining the dissociation constant for the weak electrolyte in the electric field is \(f^\infty\), which is found using Equation 2.105.

**Contour Plots of the Equilibrium Distribution Function**

Figures 2.7, 2.8 and 2.9 show representative solutions for the distribution function at equilibrium.
Figure 2.7a. The distribution function at $z=0$ plotted as a function of position along the x-axis for $b = 0.0$ and $\alpha = 0.810$.

Figure 2.7b. The contour plot of the distribution function for $b = 0.0$ and $\alpha = 0.810$. 
Figure 2.8a. The distribution function at $z=0$ plotted as a function of position along the x-axis for the case of $b = 0.1$ and $\alpha = 0.810$.

Figure 2.8b. The contour plot of the distribution function for the case of $b = 0.1$ and $\alpha = 0.810$. 
Figure 2.9a. The distribution function at $z=0$ plotted as a function of position along the $x$-axis for the case of $b = 1.0$ and $\alpha = 0.810$.

Figure 2.9b. The contour plot of the distribution function for the case of $b = 1.0$ and $\alpha = 0.810$.

Streamline Plots

To help visualize the results, stream functions were plotted for representative solutions. The continuity equation given by Equation 2.31 can be simplified using the definition of the flux given by Equation 2.64 as
\[ \nabla \cdot \mathbf{j} = 0. \quad (2.110) \]

We then define a vector stream function as
\[ \Psi = \left( 0, 0, \frac{y}{\sqrt{1 - t^2}} \psi \right). \quad (2.111) \]

In Equation 2.111, \( \psi \) is the scalar stream function. The factor \( \frac{y}{\sqrt{1 - t^2}} \) was chosen so that the streamlines are perpendicular to the direction of the flux. Mathematically, this can be seen as
\[ \mathbf{j} = \nabla \times \Psi. \quad (2.112) \]

The component of the flux in the \( y \)-direction is then
\[ J_y = y^2 \frac{\partial \psi}{\partial t}, \quad (2.113) \]
which is proportional to the derivative of the stream function with respect to \( t \). The component of the flux in the \( t \)-direction is then
\[ J_t = -\frac{y^3}{\sqrt{1 - t^2}} \frac{\partial \psi}{\partial y}, \quad (2.114) \]
which is proportional to the derivative of the stream function with respect to \( y \). The component of the flux in the \( \phi \)-direction is given by
\[ J_\phi = 0. \quad (2.115) \]

Since \( J_y \propto \frac{\partial \psi}{\partial t} \) and \( J_t \propto \frac{\partial \psi}{\partial y} \), the flux lines are perpendicular to lines of constant values of the stream function.

With Equation 2.64, the component of the flux in the \( y \)-direction is
\[ J_y = \exp \left( \frac{1}{2} y + b \frac{t}{y} \right) \left( \phi \left( \frac{1}{2} y^2 - bt \right) - y^2 \frac{\partial \phi}{\partial y} \right) + f^\infty (y^2 - 2bt). \quad (2.116) \]

The component of the flux in the \( t \)-direction is then
\[ J_t = \sqrt{1 - t^2} \exp \left( \frac{1}{2} y + b \frac{t}{y} \right) \left( b \phi - y \frac{\partial \phi}{\partial t} \right) + f^\infty 2b \sqrt{1 - t^2}. \quad (2.117) \]

The component of the flux in the \( \phi \)-direction is given by
\[ J_\phi = 0. \quad (2.118) \]

To solve for the stream function, one integrates numerically. To obtain the solution in the \( t \)-direction, Equation 2.113 was combined with Equation 2.116 and integrated in \( t \). To obtain the solution in the \( y \)-direction, Equation 2.114 was combined with Equation 2.117 and integrated in \( y \). It is of interest to point out that the boundary condition given by Equation 2.73 combined with Equation 2.113 leads to
\[ \psi \big|_{t=1} - \psi \big|_{t=-1} = 0. \quad (2.119) \]

The streamline plots are given in Figures 2.10 and 2.11. The values of the stream function are given by \( \psi = \frac{3}{4} bn^2 \) for integer values of \( n \). The choice of \( \frac{3}{4} b \) is somewhat arbitrary, one would like to put enough streamlines in the figure to make it informative and clear. However, the \( n^2 \) was not chosen arbitrarily. The space between two streamlines form a corridor with a cross section proportional to the square of the \( z \)-coordinate. The use of \( n^2 \) then means that the flow between two stream functions is proportional to the cross sectional area.
Figure 2.10. The streamlines, curves of constant $\psi$, are plotted for the case of $b = 0.1$ and $\alpha = 0.810$.

Figure 2.11. The streamlines, curves of constant $\psi$, are plotted for the case of $b = 1.0$ and $\alpha = 0.810$.

Increase in the Dissociation Equilibrium Constant

The numerical solutions show an increase in the dissociation of a weak electrolyte in the presence of an electric field. The increase in the dissociation constant is plotted for various
values of the parameter $\alpha$ in Figure 2.12. Figure 2.12 is a plot of the base ten logarithm of the ratio of the dissociation constant to the dissociation constant at zero applied electric field as a function of the strength of the applied electric field as the dimensionless parameter $b$. Figure 2.12 shows that, as the value of $\alpha$ increases, the increase in dissociation due to the applied electric field increases. It is seen that at larger values of $b$, the dimensionless strength of electric field, the dissociation equilibrium constant becomes highly dependent on the value of $\alpha$, the dimensionless bond length. This is because the strength of the Coulombic attraction between the two charges decreases at larger bond lengths.

![Figure 2.12](image)

**Figure 2.12.** The increase in the dissociation constant is plotted as a function of $b$ for various values of $\alpha$.

**Recombination Rate Constant**

The recombination rate constant can also be determined as a function of the applied electric field. This analysis assumes that the recombination reaction remains a collision controlled reaction. To solve for the recombination rate constant, one must determine the distribution function by solving Equation 2.66 with the boundary conditions given by Equation 2.69 and Equation 2.70. The distribution function will then be used with the continuity equation to determine the recombination rate constant. Rewriting the continuity equation, Equation 2.34, in terms of the recombination rate constant yields
The distribution function can be solved for using the same Fortran program as was used to determine functions $S_n$ and $T_n$, as well as the eigenvalues. For given values of $b$ and $\alpha$, the values of the functions $S_n$ and $T_n$, as well as the eigenvalues are the same as for the equilibrium case. Figures 2.5 and 2.6, as well as Table 2.1 are the same for the case of recombination. Using these functions and the boundary condition of Equation 2.69, the constants in Equation 2.76 can be determined by taking advantage of the orthogonality of the functions $T_n$. Multiplying both sides of Equation 2.76 by $T_n$, integrating from $-1$ to $1$ in $t$, and evaluating the expression at $y = \alpha^{-1}$ yields

$$c_n = -\frac{\int_{-1}^{1} T_n \exp\left(-\frac{1}{2\alpha} - b\alpha t\right) dt}{\int_{-1}^{1} T_n^2 dt}.$$  \hspace{1cm} (2.121)

With Equation 2.121, the series given by Equation 2.76 and the relation between $\phi$ and $f$ given by Equation 2.74, Equation 2.120 becomes

$$\frac{k_{-\delta}}{4\pi \ell (D_i + D_j)} = 1 + \sum_n B_n X_n.$$  \hspace{1cm} (2.122)

In Equation 2.122, the functions $B_n$ and $X_n$ are given by Equation 2.108 and Equation 2.109 respectively.

The numerical results for Equation 2.122 are plotted in Figure 2.13. It can be seen in Figure 2.13 that the recombination rate constant is a constant when $\alpha = 0$. However, when $\alpha > 0$, the recombination rate constant is seen to increase with increasing electric field. The recombination rate constant for the case $b = 0$ varies with the value of $\alpha$ as given by Equation 1.175.
Empirical Correlation of Numerical Results

The numerical solutions were fitted with an empirical correlation to ease the use of the numerical solution. Rather than solving the governing equations, future researchers can use the empirical correlation to estimate the expected recombination rate constant and dissociation rate constant. The correlation for the recombination rate constant is

$$\frac{k_{\text{-g}}}{4\pi\ell(D_i + D_j)} = \frac{2}{1 - \exp\left(-\frac{1}{\alpha}\right)} + \alpha^2 b + (4.97\alpha) \frac{\sinh(0.0835ab)}{\cosh(0.0835ab)^2}. \quad (2.123)$$

The values of 4.97 and 0.0835 were found using a least-squares fit of the numerical results. The correlation for the dissociation rate constant is given by

$$\frac{k_\delta}{k_\delta^0} = \left(\sum_{m=0}^{\infty} \frac{1}{m! (m + 1)!} (2b)^m \cosh(\tau b) \cosh(\tau)^b. \quad (2.124)$$

In Equation 2.124, $k_\delta$ is the dissociation rate constant, $k_\delta^0$ is the dissociation rate constant when $b = 0$, and $\tau$ is given by

$$\tau = -0.128 \ln(\cosh(0.235\alpha)) + 5.72\alpha^2 \quad (2.125)$$

In Equation 2.125 the values of $-0.128$, 0.235 and 5.72 were determined by a least squares fit of the numerical results. The rate constants given in Equation 2.123 and Equation 2.124 are related to the dissociation equilibrium constant by

$$K = \frac{k_\delta}{k_{\text{-g}}}. \quad (2.126)$$
Experimental Measurements

Experimental data for the dissociation of pure water in an applied electric field are lacking. The reason for the lack of data is because the measurements of the second Wien effect involve differencing techniques. The conductivity of the weak-electrolyte solution is measured in comparison to the conductivity of a strong-electrolyte solution. The concentration of the strong electrolyte is set such that the conductivity of the strong-electrolyte solution matches that of the weak electrolyte solution. Unfortunately, in the case of pure water it is impossible to form an aqueous strong electrolyte solution that matches the conductivity of pure water.

The only data on the dissociation of water in large electric fields known to the author is a single data point of Eigen and De Maeyer. In 1955, Eigen and De Maeyer published their measurement of the rate constant for the recombination of hydronium and hydroxide ions. The experiment was conducted by temporarily applying a large electric field to pure water. Following the second Wien effect, the large electric field increased the dissociation of the water. When the large electric field was then removed, the dissociation equilibrium decreased, and the ions recombined. By measuring the decay of the conductivity of the solution, Eigen and De Maeyer were able to measure the rate at which the ions recombined and thus the recombination rate constant. In 1967, Eigen shared the Nobel Prize in Chemistry for his work on measuring fast chemical reactions including the recombination of hydronium and hydroxide ions.

In a figure caption, Eigen and De Maeyer report that the conductivity increased by about 3% in a field of 70 kV/cm. The 70 kV/cm field corresponds to a dimensionless field of \( b = 0.096 \). For this electric field, the conductivity is predicted to increase 4.8% with \( \alpha = 0.0 \) or predicted to increase 6.5% with \( \alpha = 1.621 \). Regardless of the choice of \( \alpha \), the theoretically predicted increase in the conductivity is larger than the number reported by Eigen and De Maeyer. Rather than try to reconcile this difference, I choose to take the data as a qualitative measure of the increase in the conductivity. This is justified because Eigen and De Maeyer were not trying to measure directly the increase in the dissociation due to the applied electric field. Rather, they just mentioned in passing that the increase in the conductivity was "about" 3%.

Although there is a lack of data on the dissociation of water in an applied electric field, there are data on the dissociation of other weak electrolytes in an applied field. One would expect that the dissociation of weak acids and bases in aqueous solution would follow the same series of steps proposed in Equation 2.1. For example, one can break the dissociation of acetic acid up into a series of steps similar to that proposed for the dissociation of water in Figure 2.1. A similar scheme to the dissociation of water in Figure 2.1 is displayed in Figure 2.14 for acetic acid.
Figure 2.14. The dissociation of an acetic acid molecule following the scheme proposed in Equation 2.1. The different configurations in the figure correspond to the species as: configuration I to (AB), configuration II to (AB)$^\ddagger$, configuration III to $A^+ \cdots B^-$, configuration IV to $A_a^+ B_a^-$, and configuration V to $A^+$ and $B^-$. 
The increased dissociation of acetic acid in large electric fields was investigated by Schiele in 1932. The data of Schiele were used by Onsager for comparison with his theory in 1934. The data of Schiele are compared with the theory presented in this chapter in Figure 2.15. The line corresponding to $\alpha = 0.0$ is identical to the results of Onsager.

![Graph showing the increase in conductivity of an acetic acid solution](image)

**Figure 2.15.** The increase in conductivity of an acetic acid solution, expressed as a percent change in conductivity, as a function of the strength of the applied electric field. At low fields, the conductivity of the solution used in the measurement is $\kappa = 2.0 \times 10^{-4} \, \Omega^{-1} \, \text{cm}^{-1}$. The solution for $\alpha = 0.0$ is seen to fall slightly below the data at large electric fields. However, the solution for $\alpha = 0.810$ is larger than the experimental data at large electric fields.

Figure 2.15 shows that as the value of $\alpha$ is increased that the theory predicts a greater increase in the conductivity of the solution. The solution for $\alpha = 0.0$ is seen to fall slightly below the data at large electric fields. However, the solution for $\alpha = 0.810$ is larger than the experimental data at large electric fields.

There is a discrepancy between the experimental data and the theory as the applied electric field approaches zero. This discrepancy has been previously explained by Onsager. The discrepancy is due to neglecting the Debye-Hückel ion cloud in the theoretical treatment, specifically in equations such as Equation 2.16. At zero applied electric field, the ions have Debye-Hückel ion clouds surrounding them. The ion clouds screen the Coulomb attraction between two reacting ions and decreases the work required to separate the ions.

Onsager partially accounted for the effect of the ion clouds through the use of the activity coefficient as predicted by Debye-Huckel theory. Using this activity coefficient, Onsager
calculated the deviation of his theory from the experimental data at zero applied electric field. The lines in Figure 2.15 are adjusted using the method of Onsager.

To calculate the adjustment used by Onsager for the lines in Figure 2.15, one begins with the expression for the activity coefficient from Debye-Hückel theory. The activity coefficient can be expressed as

$$\ln \gamma_i = -\frac{z_i^2e^2}{8\pi\varepsilon k_BT} \frac{1}{\lambda + \frac{a_i}{\lambda}}$$

(2.127)

In Equation 2.127, \(\gamma_i\) is the activity coefficient of species \(i\) and \(\lambda\) is the Debye length as given by Equation 1.46. The reaction equilibrium is then related to the equilibrium constant and the activity coefficients by

$$\frac{c_+^0 c_-^0 \gamma_+^0 \gamma_-^0}{c_{+-}^0 \gamma_{+-}^0} = K^0.$$  

(2.128)

In Equation 2.128, \(c_+^0\) is the concentration of positively charged ions when the applied field is zero, \(c_-^0\) is the concentration of negatively charged ions when the applied field is zero, and \(c_{+-}^0\) is the concentration of neutral molecules when the applied field is zero. All concentrations in Equation 2.128 are bulk concentrations. The equilibrium constant, \(K^0\), in Equation 2.26 is the same as the equilibrium constant, \(K^0\), in Equation 2.128.

At large electric fields, Onsager recognizes that the Debye-Hückel ion clouds will be destroyed, causing the activity coefficients to approach unity. Under the conditions of a large electric field, the reaction equilibrium expression is then

$$\frac{c_+ c_-}{c_{+-}} = K.$$  

(2.129)

In Equation 2.129, the equilibrium constant \(K\) is the same as the equilibrium constant \(K\) in Equation 2.128 in the limit of large electric fields.

The relation between the change in conductivity and the electric field can now be derived. Electroneutrality is assumed so that \(c_+ = c_-\). The material balance relating the concentration of species at zero applied electric field to the concentration of species at non-zero electric field is given by \(c_{+-}^0 + c_+^0 = c_{+-} + c_+\). For a binary electrolyte in an electrically neutral region, the conductivity is given by

$$\kappa = \frac{F^2}{RT} \left( c_+ \right).$$

(2.130)

In Equation 2.130, \(\kappa\) is the conductivity. Combination of Equation 2.128, Equation 2.129, Equation 2.120, the electroneutrality assumption, and the material balance yields

$$\frac{\kappa - \kappa^0}{K^0} = -\frac{1}{2} K^0 \left( \frac{K}{K^0} \right) + \frac{1}{4} K^0 \left( \frac{K}{K^0} \right)^2 + \frac{1}{c_+^0} \left( \frac{c_+^0}{c_+^0} + 1 \right) \left( \frac{K}{K^0} \right) - 1.$$  

(2.131)

Equation 2.131 relates the change in the conductivity to the change in the equilibrium constant due to the applied electric field. Equation 2.131 is used to produce the lines on Figure 2.15.

If one were interested in calculating the expected change in conductivity at low applied electric fields, as \(E \to 0\) in Figure 2.15, one would need to include the effects of the Debye-Hückel ionic atmosphere. To include the atmosphere, one would need to replace the potential used in Equation 2.16 and Equation 2.17 with one found by solving Poisson's equation. The distribution functions would need to include \(f_{ij}\) as well as \(f_{ji}\).
Choice of $\alpha$

The only adjustable parameter in the theory presented in this chapter is $\alpha$. The parameter $\alpha$ represents the bond length at which the ions separate and begin to diffuse apart from one another. The effect of changing $\alpha$ can be seen in Figures 2.12 and 2.13. Ideally, $\alpha$ could be measured directly, and then there would be no free parameters present in the theory. As far as the author is aware, the direct measurement has not been performed. The measurement of $\alpha$ would need to be a direct measurement of the number of hydrogen bonds that separate the charges when water splitting occurs.

One way to get an indirect measurement of $\alpha$ is to measure the recombination rate constant. Using the theory presented in Chapter 1, the rate of recombination for a collision-controlled reaction can be related to the distance at which the chemical bond is formed. The distance of interest is the $\alpha$ in Equation 1.178. The difficulty is that the geometry factor, $\theta$ in Equation 1.178, must be estimated. Usually, authors simply assume that $\theta = 1$. Unfortunately, this assumption leads to inconsistencies. For example, the rate of recombination for hydronium ions and acetate ions was reported by M. Eigen and J. Schoen in 1955 [M. Eigen and J. Schoen]. If it is assumed that $\theta = 1$, then the measured rate of recombination is slower than that predicted with a bond length of 0.0 nm. Thus, the geometry factor for the recombination of hydronium and acetate ions cannot equal 1. However, once the geometry factor is allowed to vary from 1, there are two adjustable parameters for a single data point. The problem is no longer constrained, and the two parameters must be estimated intuitively. For example, if the site of protonation on a weak acid is half obstructed by the rest of the weak acid molecule, it could be approximated that $\theta = \frac{1}{2}$.

The rate of recombination of hydronium ions and hydroxide ions has been measured by multiple authors.\textsuperscript{9,16} If it is assumed that the geometry factor in Equation 1.178 is equal to 1, then the measured rate of recombination corresponds to a bond length of 0.58 nm or $\alpha = 0.810$. In discussion of the many results of collision-controlled reactions, Eigen and De Maeyer speculate that the geometry factor for the recombination of hydronium ions and hydroxide ions should be about 0.75.\textsuperscript{17} They further estimate that the actual recombination distance for hydronium ions and hydroxide ions should fall between 0.75 nm and 1.25 nm or $1.05 < \alpha < 1.75$.\textsuperscript{17}

A second approach to determining the value of $\alpha$ is through molecular modeling. Modeling the recombination of hydronium and hydroxide ions was first attempted by Geissler et al. in 2001.\textsuperscript{10} Due to the computational complexity of the problem, they were able to simulate only 32 water molecules. They found that the bond length during the recombination reaction was at least 0.6 nm. However, due to the computational limitations, they were not able to probe greater lengths.

The problem of modeling the recombination of hydronium and hydroxide ions was revisited by Hassanali et al. in 2011.\textsuperscript{18} Due to improvements in computation, they were able to simulate 64 water molecules. They interpret their results to suggest that the recombination distance is about 0.6 nm. However, they state that when the ions were separated by greater distances, they still recombined more rapidly than would be suggested by diffusion. The
authors attribute this to an effect of enhanced diffusion when the ions are separated by about 1 nm. The authors were not able to probe distances greater than 0.8 nm.

In light of all of these results, it seems reasonable to assume that the bond length in the dissociation of water is between 0.58 nm and 1.25 nm. This corresponds to values of $0.810 < \alpha < 1.75$.

**Conclusion**

The dissociation of weak electrolytes increases in an applied electric field. The increase in dissociation can be attributed to two effects: 1. Charge separation along an undissociated weak-electrolyte molecule is energetically more favorable in the presence of an electric field. 2. The ions resulting from dissociation are less likely to recombine because the applied electric field overcomes the Coulomb attraction between the pair of ions and drives them apart.

The two effects of the applied electric field on the dissociation can be seen in Figures 2.7 through 2.11. In Figures 2.7 through 2.9 it is seen that the distribution at the bond length deforms, following a Boltzmann distribution. This deformation leads to a decrease in the distribution function at negative values of the x-coordinate and an increase in the distribution function at positive values of the x-coordinate. Due to the statistical weighting, the net result is that the distribution function at the bond length increases. Thus, the electric field is favoring the charge-separated state. By comparing Figures 2.10 and 2.11 it is seen that the larger electric field produces streamlines that show smaller perturbations near the central ion. This means that the Coulomb attraction between the ions is less important when the electric field is larger. Thus, the electric field is overcoming the Coulomb attraction and driving the free ions apart.

The results presented here account for a range of physically plausible bond lengths. This is an extension of the classic work of Onsager which accounts only for a bond length of zero. As seen in Figure 2.12, the larger bond lengths lead to predicted dissociation constants that differ by orders of magnitude.

The strength of the electric field necessary to observe the difference between various bond lengths is very large. The data displayed in Figure 2.15 are typical of data for a weak electrolyte in an aqueous solution. However, as is seen in Figure 2.15, it is difficult to determine which bond length fits the data best. One cannot perform the same experiment as was done to obtain the data in Figure 2.15 because dielectric breakdown of the solution will occur at larger electric fields. It is predicted that the large electric fields necessary to observe the large increase in the dissociation of weak electrolytes will be present at interfaces. It is believed that by studying the properties of weak electrolytes at these interfaces one could obtain the bond length.

**Notation**

- $a$: Closest distance of approach of the ions before reaction occurs
- (AB): Undissociated weak electrolyte molecule in a random orientation
- (AB)$^\dagger$: Undissociated weak electrolyte molecule in an orientation allowing dissociation
- $A^+$: Cation
- $A^+\cdots B^-$: Undissociated weak electrolyte molecule with charge separation
- $A^+_a B^-_a$: Pair of dissociated ions at a separation of $a$
- $A_n$: Grouping of parameters
b  Dimensionless strength of the electric field
B−  Anion
Bn  Grouping of parameters
cx  Constant coefficient of term x
D_i  Diffusivity
e  Elementary charge of a proton
E  Applied macroscopic electric field
f_\infty  Dimensionless distribution function at infinity
f_{ji}  Distribution function
G  Electric field experienced by the molecule locally
g_x  Degeneracy of species x
J_{1}  The ordinary Bessel function of order 1
J  Dimensionless flux
K  Equilibrium constant
k_B  Boltzmann constant
k_{\alpha}  Forward reaction rate constant of step \alpha
k_{-\alpha}  Reverse reaction rate constant of step \alpha
l  Bjerrum length
n  Index of refraction
n  Outward normal unit vector
N  Flux of the distribution function
n_x  Macroscopic concentration of species x
P_x  Legendre polynomial of order x
Q_x  Deviation of the xth function from P_x
R  Dimensionless radial position
S_x(R)  xth function of R
t  cos \theta
T  Absolute temperature
T_x(t)  xth function of t
U_{ij}  Potential energy of an ion of type j near an ion of type i
U_x  Potential energy associated with species x
v_{ij}  Velocity of ions of type j near an ion of type i
X_n  Grouping of terms
y  R^{-1}
z_i  Number of elementary charges carried by an ion of type i
\alpha  Dimensionless distance of charge separation
\beta  Parameter reflecting the strength of the electric field
\varepsilon  Dielectric permittivity
\varepsilon_0  Permittivity of free space
\theta  Angle between the local field and a vector pointing from the negative charge to the positive charge
\mu_x  xth eigenvalue
\nu_x  Deviation of the xth eigenvalue from x(x + 1)
\( \xi \)  
Factor of order unity accounting for the difference between \( G \) and \( E \)

\( \tau \)  
A small parameter equal to \( 1 + t \)

\( \varphi \)  
Scaled distribution function

\( \Phi_i \)  
Electrostatic potential near an ion of type \( i \)

\( \omega \)  
A small parameter equal to \( 1 - t \)

\( \psi \)  
Scalar stream function

\( \Psi \)  
Vector stream function
Chapter 3: Modeling the Electrochemical Behavior of Bipolar Membranes

Abstract

A 1-d continuum model of a bipolar membrane is shown. The model accounts for the diffusion and migration of species, electrostatics, and chemical reaction. The bipolar membrane model is seen to rectify current and undergo breakdown. This is the first model to use a model of water splitting at large electric fields to predict the breakdown of the junction. A layer of weak base is included in the junction of the membrane as a catalyst layer. Model results show agreement with published experimental results. The effect of the catalyst layer is seen to be negligible. The ineffectiveness of the catalyst is attributed to the greater increase in water dissociation due to the electric field than by the catalyst mechanism. Results are shown for a bipolar membrane immersed in a neutral pH solution as well as a bipolar membrane separating a solution with a pH of 2 from a solution with a pH of 12.

Introduction

A bipolar membrane consists of an adjacent cation-exchange layer and anion-exchange layer. The ion-exchange layers are usually composed of polymers containing fixed charge groups. Each layer is usually about 50 μm thick. The charge groups in the cation-exchange layer are of a strongly acidic type, such as a sulfonic acid group $-\text{SO}_3^-$. The charge groups in the anion-exchange layer are of a strongly basic type, such as a quaternary ammonium group $-\text{NR}_3^+$. The concentration of fixed charge groups in either membrane is typically about 1 M. A catalyst layer is often introduced between the two ion-exchange membranes. This catalyst layer is usually 2 to 10 nm thick. The catalyst layer usually consists of weakly acidic or weakly basic groups fixed to a polymer backbone. A possible weakly basic group for inclusion in the catalyst layer is a tertiary amine $-\text{NR}_2$, which can be converted into the conjugate acid $-\text{NR}_2\text{H}^+$. When a bipolar membrane is immersed in an aqueous electrolyte, it swells with water. The ions in the membrane undergo ion exchange with the ions in solution. The equilibrium concentration of the ions in the bulk of the membrane is equilibrated with the ions in the adjacent solution following Donnan equilibrium. Under typical conditions, this leads to a cation-exchange layer with a large concentration of mobile cations and a small concentration of mobile anions. Similarly, the anion-exchange layer will contain a large concentration of mobile anions and a small concentration of mobile cations. The junction of a bipolar membrane is thought of as the region near where the two membranes come together. The junction is usually about 20 nm thick. At equilibrium, the junction region is depleted of mobile ions. The depletion of mobile ions leads to interesting behavior when ionic current is passed through the membrane.

The bipolar membrane is of both commercial and academic interest because of how current passes through the membrane. There are two directions in which current can be passed through a bipolar membrane: in the direction of forward bias, and in the direction of reverse bias. In the direction of forward bias, current passes through the membrane such that both the cations in the cation-exchange layer and the anions in the anion-exchange layer are moving towards the junction region. In the direction of reserve bias, the current passes through the membrane such that both the cations in the cation-exchange layer and the anions in the anion-exchange layer are moving away from the junction region. In the direction of forward bias,
concentration of ions in the junction region increases, and the overall resistance of the membrane decreases. In the direction of reverse bias, the concentration of ions in the junction region decreases, and the resistance of the bipolar membrane increases. The decrease of mobile ions in the junctions leads to a limiting current. Interestingly, if a further bias is applied, the junction of the bipolar membrane eventually undergoes "breakdown." When breakdown occurs, the resistance of the membrane decreases. It is observed that under breakdown the current through the bipolar membrane is carried by hydronium and hydroxide ions.

Breakdown of the bipolar membrane is especially of interest because most commercial applications of bipolar membranes take advantage of breakdown. During breakdown, the water splitting reaction occurs rapidly. This reaction can be written as

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-.$$  \hspace{1cm} (3.1)

The dissociation reaction given in Equation 3.1 has \(\Delta_{\text{rxn}}G^0 = 79.885 \text{ kJ mol}^{-1}\) and \(\Delta_{\text{rxn}}H^0 = 55.836 \text{ kJ mol}^{-1}\). This reaction is of commercial interest in the production of acids and bases and other ion exchange processes. When the water-dissociation reaction occurs in a bipolar membrane, it is also of academic interest. This is because the reaction occurs at billions of times the rate that it occurs in a solution of pure water. The cause of the increase of the rate of this reaction has been poorly understood.

Bipolar membranes can be used for bipolar-membrane electrodialysis. In bipolar-membrane electrodialysis, current is passed through a stack of ion-exchange membranes, including bipolar membranes, in order selectively to add and remove ions from aqueous solutions. Bipolar-membrane electrodialysis can be used to produce an acidic solution and a basic solution from salt solutions. Figure 3.1 is a diagram of the use of bipolar-membrane electrodialysis for the production of an acidic and a basic solution. The ion-exchange membranes are arranged in a stack of repeated units to maximize efficiency. The total number of ion-exchange membranes between the electrodes is often 100 or greater. The electrodes are not shown in Figure 3.1. Typically, the cathode will evolve hydrogen gas, and the anode will evolve oxygen gas. The efficiency of the electrode reactions is usually not an important part of the overall efficiency of the electrodialysis process since there are so many ion-exchange membranes between the electrodes.

Electrodialysis with bipolar membranes is not yet a commercially viable technology. Most knowledge of bipolar membranes comes from laboratory-scale experiments. The process is not currently economically viable due to shortcomings in the performance of the ion-exchange membranes. The problems include degradation of the membranes and the operating cost of the process. It is hoped that how the bipolar membranes function can be understood through quantitative modeling. This knowledge could then be used by researchers to design better bipolar membranes.
Figure 3.1. A process for bipolar-membrane electrodialysis. The process is able to produce an acidic solution and basic solution while depleting a salt solution by passing current through a stack of ion-exchange membranes. The gray areas represent aqueous electrolyte. The part of the process shown in the dashed box is a repeated unit.

Experimental Behavior of Bipolar Membranes

Laboratory experiments have been used to probe the behavior of bipolar membranes. The most important experiment is the creation of an i-V curve. This is done by passing current through a bipolar membrane while measuring the potential drop across the bipolar membrane using a pair of reference electrodes. The typical experimental setup is shown in Figure 3.2.
Figure 3.2. The experimental setup used to measure the current-voltage behavior of a bipolar membrane. Current is passed between the working electrodes as the potential is measured between reference electrodes placed across the bipolar membrane. The additional anion-exchange membrane and the cation-exchange membrane are used to help keep the composition in the solutions adjacent to the bipolar membrane constant during the course of the experiment.

It is important to mention the sign convention that is used when describing the potential across a bipolar membrane. The sign convention used here follows that of the majority of the bipolar-membrane literature. This sign convention follows that of the semiconductor literature rather than the electrochemical-engineering literature. The convention is to orient the bipolar membrane such that the cation-exchange region is on the left of the anion-exchange region. The reported potential across the bipolar membrane is then the potential of the reference electrode on the left minus the potential of the reference electrode on the right.

Typical results for an i-V curve of a bipolar membrane are shown in Figure 3.3. The i-V curve displays three regions of interest. The first region is for positive potentials, also known as a positive bias. In this region the current density increases rapidly with applied voltage. Here the current is predominantly carried by the ions present in the adjacent electrolyte. The other two regions are for negative potentials, or negative bias. The second region is for negative potentials extending from 0 to -0.5 V. This region is the limiting current region. In this region the current is being predominantly carried by ions present in the adjacent electrolyte. However, a limiting current behavior is seen. Further decreases in the potential between the reference
electrodes does not lead to a change in the current density. The last region is the breakdown region. This region occurs at potentials less than -0.5 V. Here the current density rapidly becomes more negative with further decrease in the applied potential. In this region, the current is being carried predominately by H$_3$O$^+$ and OH$^-$ ions.

**Figure 3.3.** A typical i-V curve of a bipolar membrane. The current density through the membrane is plotted as a function of the potential of the left reference electrode minus the right reference electrode where the two reference electrodes are immediately adjacent to the bipolar membrane. The aqueous electrolyte is 0.1 M Na$_2$SO$_4$.\textsuperscript{5}

**Model Geometry**

The model treats a one-dimensional slice through the bipolar membrane and the adjacent solution. The model attempts to capture the experimental setup in Figure 3.2. The model divides the system into five different layers. The chief difference in the different layers is the presence of fixed charge groups and a change in the concentration of water. The bipolar
membrane is treated as three layers: a cation-exchange layer, an anion-exchange layer, and a catalyst layer located between the cation-exchange layer and the anion-exchange layer. The other two layers are Nernst stagnant diffusion layers located on either side of the bipolar membrane. The cation-exchange layer and the anion-exchange layer are both 50 µm thick. The catalyst layer is 10 nm thick. The Nernst stagnant diffusion layers are each 30 µm thick. A diagram of the model geometry is shown in Figure 3.4.

**Figure 3.4.** The geometry for the bipolar membrane model consists of five layers. The layers, from left to right, are a Nernst stagnant diffusion layer of aqueous solution, the cation-exchange layer, the catalyst layer, the anion-exchange layer, and finally a Nernst-stagnant-diffusion layer of aqueous solution.

**Model Species**

There are several different species within a bipolar membrane. For this model, nine different species are considered: \( \text{H}_2\text{O}, \text{H}_3\text{O}^+, \text{OH}^-, \text{Na}^+, \text{SO}_4^{2-}, \text{M}^+, \text{M}^-, \text{NR}_2, \text{and} \text{NR}_2\text{H}^+. \) The water molecules, \( \text{H}_2\text{O}, \) are treated as being present at a concentration that is a fixed value at each location in the model. The fixed concentration of water assumes that water cannot be depleted at any point in the model. The concentration of water in the ion-exchange membranes is less than the concentration of water in the stagnant diffusion layers. The hydronium ions, \( \text{H}_3\text{O}^+, \) and the hydroxide ions, \( \text{OH}^- \), are allowed to move through the system following Nernst-Planck type diffusion equations. Additionally, the homogeneous dissociation of water into hydronium and hydroxide is included in the model. The sodium ions, \( \text{Na}^+ \), and the sulfate ions, \( \text{SO}_4^{2-} \), are also allowed to move through the system following the Nernst-Planck type diffusion equations. Bisulfate ions, \( \text{HSO}_4^- \), are not included in the model.
The concentration of the anion-exchange layer, $M^+$, is set at every location in the model. The anion-exchange groups are immobile and dissociated. Similarly, the concentration of the cation-exchange layer, $M^-$, is set at every location in the model. The cation-exchange groups are immobile and dissociated.

In addition to the cation-exchange layer and the anion-exchange layer, there is a catalyst layer in the bipolar membrane. The catalyst layer is usually about 10 nm of weak-base groups.²,⁵ This layer is included because the weak-base groups are thought to aid in the dissociation of water through a catalytic reaction. The catalytic weak-base groups can either be a deprotonated weak-base group, $-NR_2$, or a protonated weak-base group, $-NR_2H^+$. Both $-NR_2$ and $-NR_2H^+$ are immobile. The weak-base groups participate in homogeneous chemical reactions in which $-NR_2$ is protonated and $-NR_2H^+$ is deprotonated. The total concentration of the weak-base groups and protonated weak-base groups is set at each location in the model. The relative concentration of $-NR_2$ and $-NR_2H^+$ depends on the material balances of those species.

Electrochemical Potentials

Expressions for the electrochemical potentials of the various species are used to construct a thermodynamically consistent model. In a bipolar membrane, the electrochemical potential of a species is a function of temperature, pressure, composition, electrostatic potential, and electric field. The temperature dependence is included in the expressions for the electrochemical potentials. It is assumed that the model is isothermal, and thus heat transfer is not included. The pressure is assumed to be 1 bar. The composition is solved as a function of position in the model. The electrostatic potential is determined as a function of position in the model. The electrostatic potential is determined by solving Poisson’s equation.

The electrochemical potentials are also a function of the electric field. Most treatments of electrochemical systems do not include a electrochemical potential that is a function of the electric field. The electric-field-dependent term is included here because in Chapter 2 the dissociation and recombination rate constants as well as the dissociation equilibrium constant are functions of the electric field. Since the dissociation equilibrium constant, a thermodynamic quantity, is a function of the electric field, then the electrochemical potentials must be functions of the electric field.

The expressions for the electrochemical potentials follow the form given by Newman.⁷ The same reference state is used for a given species for all locations of the species in the model. This means that the same reference state is used for both the aqueous phase and the membrane phase.

Two different reference states are used. The water molecules are treated as the solvent. The water molecules are therefore referenced to pure liquid water under standard conditions. The ions $H_3O^+$, $OH^-$, $Na^+$, $SO_4^{2-}$, $-NR_2$, and $-NR_2H^+$ are treated as being dilute species in water. These species are referenced to a secondary reference state such that at infinite dilution the activity coefficient approaches 1. The tabulated reference quantities are for an aqueous solution with concentrations in molal units under standard conditions with an arbitrary choice of $\mu_{H^+}^0 = 0.3$. The electrochemical potential of the membrane species, $M^+$ and $M^-$, do not appear in the model. Equations 3.2 through 3.8 lay out the expressions for the electrochemical potentials for the species $M^+$ and $M^-$. 
potentials. Explaining the full meaning of the forms of the electrochemical potential used in Equations 3.2 through 3.8 will take the next few sections.

The electrochemical potential of the water molecules is given by

$$\mu_{H_2O} = \mu_{H_2O}^0.$$  \hspace{1cm} (3.2)

The electrochemical potential of the hydronium ions is given by

$$\mu_{H_3O^+} = \mu_{H_3O^+}^0 + RT \ln \left( \frac{c_{H_3O^+}^0}{c_{H_2O}^0} \right) + F\Phi - \frac{1}{2} RT \ln \left( \frac{k_1^E}{k_{-1}^E} \right).$$  \hspace{1cm} (3.3)

The electrochemical potential of the hydroxide ions is given by

$$\mu_{OH^-} = \mu_{OH^-}^0 + RT \ln \left( \frac{c_{OH^-}^0}{c_{H_2O}^0} \right) - F\Phi - \frac{1}{2} RT \ln \left( \frac{k_1^E}{k_{-1}^E} \right).$$  \hspace{1cm} (3.4)

The electrochemical potential of the sodium ions is given by

$$\mu_{Na^+} = \mu_{Na^+}^0 + RT \ln \left( \frac{c_{Na^+}^0}{c_{H_2O}^0} \right).$$  \hspace{1cm} (3.5)

The electrochemical potential of the sulfate ions is given by

$$\mu_{SO_4^{2-}} = \mu_{SO_4^{2-}}^0 + RT \ln \left( \frac{c_{SO_4^{2-}}^0}{c_{H_2O}^0} \right) - 2F\Phi.$$  \hspace{1cm} (3.6)

The electrochemical potential of the weak-base groups is given by

$$\mu_{R_3N} = \mu_{R_3N}^0 + RT \ln \left( \frac{c_{R_3N}^0}{c_{H_2O}^0} \right).$$  \hspace{1cm} (3.7)

The electrochemical potential of the protonated weak-base groups is given by

$$\mu_{R_3NH^+} = \mu_{R_3NH^+}^0 + RT \ln \left( \frac{c_{R_3NH^+}^0}{c_{H_2O}^0} \right) + F\Phi - \frac{1}{2} RT \ln \left( \frac{k_1^E}{k_{-1}^E} \right).$$  \hspace{1cm} (3.8)

Many symbols are used in Equations 3.2 through 3.8. The electrochemical potential of species $i$ is given by $\mu_i$. The reference state for pure water at 1 bar is given by $\mu_{H_2O}^0$. The reference state for species $i$ in water at 1 bar is given by $\mu_i^0$. Both $\mu_{H_2O}^0$ and $\mu_i^0$ are functions of temperature. The ideal-gas constant is given by R. The concentration of species $i$ in molar is given by $c_i$. The concentration of species $i$ in a 1 molal solution is given by $c_i^\theta$. The concentration of water in pure water is given by $c_{H_2O}^0$. The value of $c_{H_2O}^0$ is set to 55.34 molar. Faraday’s constant is given by F. The macroscopic electrostatic potential is given by $\Phi$. The electric field dependence of the rate constant for the dissociation reaction given in Equation 3.1 is given by $k_1^E$, and that for the recombination reaction by $k_{-1}^E$.

The use of $c_{H_2O}/c_{H_2O}^0$ in many of the expressions for the electrochemical potentials is done to account for the volume fraction of water in the membrane. The form of the electrochemical potentials assumes that to a first approximation the water-swollen membrane consists of two phases separated on microscopic length scales. The two phases are a water-rich phase and a polymer-rich phase.

The electric-field dependence of the dissociation and recombination rate constants were calculated numerically in Chapter 2. The empirical fits of the results given by Equation 2.123 and Equation 2.124 are used in the model of the bipolar membrane. The term involving
$k_1^E$ and $k_{-1}^E$ accounts for the change in the dissociation of water in an electric field. This term is important because at equilibrium in a bipolar membrane there is a nonzero electric field at the junction of the membrane. This electric field will lead to further dissociation of water.

It should be pointed out that the $1/2$ in Equation 3.3, Equation 3.4, and Equation 3.8 cannot be measured. The parameter cannot be measured because the measurement would involve measuring the properties of a system that is not electrically neutral. The factor of $1/2$ in the terms involving $k_1^E$ and $k_{-1}^E$ reflects a choice that the effect of the electric field upon the dissociation of water would change the electrochemical potential of the $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ion equally while not changing the electrochemical potential of $\text{H}_2\text{O}$. This choice was made to simplify the resulting expressions.

**Chemical Reactions**

Three bulk chemical reactions are treated in the model. The first of these is the dissociation of water into hydronium and hydroxide ions. The reaction is written as

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-.$$  \hfill (3.9)

In Equation 3.9, $k_1$ is the dissociation rate constant, and $k_{-1}$ is the recombination rate constant. Chapter 2 detailed how these rate constants are functions of the electric field. At equilibrium, the change in Gibbs free energy of reaction is zero. Combining the expressions for the electrochemical potentials given in Equations 3.2, 3.3 and 3.4 yields

$$\frac{c_{\text{H}_3\text{O}^+}c_{\text{OH}^-}}{c_{\text{H}_2\text{O}}^2} = K_1^0 \frac{k_1^E}{k_{-1}^E}.$$  \hfill (3.10)

where

$$K_1^0 = \frac{c_{\text{H}_3\text{O}^+}^0c_{\text{OH}^-}^0}{c_{\text{H}_2\text{O}}^0} \exp \left( \frac{2\mu_{\text{H}_2\text{O}}^0 - \mu_{\text{H}_3\text{O}^+}^0 - \mu_{\text{OH}^-}^0}{RT} \right).$$  \hfill (3.11)

In Equation 3.10, $K_1^0$ is the equilibrium constant at zero macroscopic electric field. It is calculated from all of the reference quantities given in Equation 3.11. The ratio $k_1^E/k_{-1}^E$ in Equation 3.10 is the effect of the electric field upon the dissociation equilibrium. This quantity was calculated Chapter 2.

The second bulk chemical reaction treated in the model is the protonation of the weak base group. The reaction is written as

$$\text{H}_2\text{O} + \text{R}_3\text{N} \rightleftharpoons \text{R}_3\text{NH}^+ + \text{OH}^-.$$  \hfill (3.12)

The weak-base groups, $\text{R}_3\text{N}$ and $\text{R}_3\text{NH}^+$, are immobile species that act as the catalysts for the water splitting reaction. At equilibrium, the change in Gibbs free energy of reaction is zero. Expressions for the electrochemical potentials given by Equations 3.2, 3.4, 3.7, and 3.8 are combined to yield

$$\frac{c_{\text{R}_3\text{NH}^+}c_{\text{OH}^-}}{c_{\text{H}_2\text{O}}c_{\text{R}_3\text{N}}} = K_2^0 \frac{k_1^E}{k_{-1}^E},$$  \hfill (3.13)

where
In Equation 3.13, $K_2^0$ is the equilibrium constant at zero macroscopic electric field. The ratio $k_1^E/k_{-1}^E$ also appears in Equation 3.13. The ratio appears because Equation 3.12 generates a pair of charges. From Chapter 2, a reaction that generates a pair of charges is a function of the electric field. The quantity $k_1^E/k_{-1}^E$ is identical to $k_2^E/k_{-2}^E$.

The third bulk chemical reaction is the deprotonation of the protonated-weak-base group. The reaction is written as

$$k_3 \quad H_2O + R_3NH^+ \rightleftharpoons H_3O^+ + R_3N. \quad (3.15)$$

At equilibrium, the change in Gibbs free energy of reaction is zero. Combining the expressions for the electrochemical potentials given by Equations 3.2 3.3, 3.7, and 3.8 yields

$$\frac{c_{H_3O^+}c_{R_3N}}{c_{H_2O}c_{R_3NH^+}} = K_3^0, \quad (3.16)$$

where

$$K_3^0 = \frac{c_{H_3O^+}c_{R_3N}}{c_{H_2O}c_{R_3NH^+}} \exp \left( \frac{\mu_{H_2O}^0 + \mu_{R_3N}^0 - \mu_{R_3NH^+}^0 - \mu_{OH^-}^0}{RT} \right). \quad (3.17)$$

In Equation 3.16, $K_2^0$ is the equilibrium constant at zero macroscopic electric field. Notice that the equilibrium given by Equation 3.16 does not depend upon the strength of the applied electric field. The equilibrium does not depend on the applied electric field because there is not a net production of charges in the reaction.

The reactions given by Equation 3.9, Equation 3.12, and Equation 3.15 are not thermodynamically independent. The reaction rate constants are related such that

$$\frac{k_1}{k_{-1}} = \frac{k_2k_3}{k_{-2}k_{-3}}.$$

**Flux Equations and Material Balances**

The fluxes of the mobile species are assumed to follow a generalized Nernst-Planck equation. The mobile species in the model are $H_3O^+$, $OH^-$, $Na^+$, and $SO_4^{2-}$. The generalized Nernst-Planck equation is

$$N_i = -D_i c_i \frac{1}{RT} \frac{d\mu_i}{dx}. \quad (3.18)$$

In Equation 3.18, $N_i$ is the flux of species $i$, and $D_i$ is the diffusion coefficient of species $i$.

Material balances for the species are also included in the model. Since the model is a steady-state model, no derivatives with respect to time appear in the material balances. The mobile species follow a material balance of

$$\frac{dN_i}{dx} = R_i. \quad (3.19)$$

In Equation 3.19, $R_i$ is the production of species $i$ through homogeneous chemical reactions.
Governing Equations

The model numerically solves 10 first-order ordinary differential equations. Four of these differential equations are found by combining the electrochemical potentials given by Equations 3.3, 3.4, 3.5, and 3.6 with the generalized Nernst Planck equation, Equation 3.18. Four additional differential equations are found by writing material balances, Equation 3.19, for each of the mobile species. The last two differential equations are from electrostatics. They are Poisson’s equation and the relation between the electric field and the electrostatic potential. All ten of the differential equations are listed below.

The first flux equation is for the flux of hydronium ions

\[ N_{\text{H}_3\text{O}^+} = -D_{\text{H}_3\text{O}^+} \frac{dc_{\text{H}_3\text{O}^+}}{dx} + D_{\text{H}_3\text{O}^+}c_{\text{H}_2\text{O}} \frac{d\ln(c_{\text{H}_2\text{O}})}{dx} \]

\[ + D_{\text{H}_3\text{O}^+}c_{\text{H}_3\text{O}^+} \frac{F}{RT} E + D_{\text{H}_3\text{O}^+}c_{\text{H}_3\text{O}^+} \frac{1}{2} \frac{d\ln \left( \frac{k_F}{k_{-1}} \right)}{dx}. \]  

(3.20)

The second flux equation is for the flux of hydroxide ions

\[ N_{\text{OH}^-} = -D_{\text{OH}^-} \frac{dc_{\text{OH}^-}}{dx} + D_{\text{OH}^-}c_{\text{OH}^-} \frac{d\ln(c_{\text{H}_2\text{O}})}{dx} - D_{\text{OH}^-}c_{\text{OH}^-} \frac{F}{RT} E \]

\[ + D_{\text{OH}^-}c_{\text{OH}^-} \frac{1}{2} \frac{d\ln \left( \frac{k_1}{k_{-1}} \right)}{dx}. \]  

(3.21)

The third flux equation is for the flux of sodium ions

\[ N_{\text{Na}^+} = -D_{\text{Na}^+} \frac{dc_{\text{Na}^+}}{dx} + D_{\text{Na}^+}c_{\text{Na}^+} \frac{d\ln(c_{\text{H}_2\text{O}})}{dx} + D_{\text{Na}^+}c_{\text{Na}^+} \frac{F}{RT} E. \]  

(3.22)

The fourth flux equation is for the flux of sulfate ions

\[ N_{\text{SO}_4^{2-}} = -D_{\text{SO}_4^{2-}} \frac{dc_{\text{SO}_4^{2-}}}{dx} + D_{\text{SO}_4^{2-}}c_{\text{SO}_4^{2-}} \frac{d\ln(c_{\text{H}_2\text{O}})}{dx} \]

\[ - 2D_{\text{SO}_4^{2-}}c_{\text{SO}_4^{2-}} \frac{F}{RT} E. \]  

(3.23)

There are also four material balances in the model. The first material balance is on hydronium ions

\[ 0 = - \frac{dN_{\text{H}_3\text{O}^+}}{dx} + k_1c_{\text{H}_2\text{O}} - k_{-1}c_{\text{H}_3\text{O}^+}c_{\text{OH}^-} + k_3c_{\text{H}_2\text{O}}c_{\text{NR}_2\text{H}^+} \]

\[ - k_{-3}c_{\text{H}_3\text{O}^+}c_{\text{NR}_2}. \]  

(3.24)

The second material balance is on hydroxide ions

\[ 0 = - \frac{dN_{\text{OH}^-}}{dx} + k_1c_{\text{H}_2\text{O}} - k_{-1}c_{\text{H}_3\text{O}^+}c_{\text{OH}^-} + k_2c_{\text{H}_2\text{O}}c_{\text{NR}_2} \]

\[ - k_{-2}c_{\text{NR}_2\text{H}^+}c_{\text{OH}^-}. \]  

(3.25)

The third material balance is on sodium ions

\[ 0 = - \frac{dN_{\text{Na}^+}}{dx}. \]  

(3.26)

The fourth material balance is on sulfate ions

\[ 0 = - \frac{dN_{\text{SO}_4^{2-}}}{dx}. \]  

(3.27)

The last two differential equations are from electrostatics. The first is Poisson’s equation
\[
\frac{d(\varepsilon E)}{dx} = F(c_{H_3O^+} - c_{OH^-} + c_{Na^+} - 2c_{SO_4^{2-}} + c_{-NR_2H^+}).
\]

(3.28)
The second is the relation between the electric field and the electrostatic potential

\[
- \frac{d\Phi}{dx} = E.
\]

(3.29)
The ten differential equations, Equation 3.20 through 3.29, constitute the governing differential equations for the model. These equations are expressed in terms of finite differences and solved numerically using a program written in Fortran using the BAND subroutine. 

In addition to the differential equations, two algebraic equations are solved. The algebraic equations are material balances for determining \(c_{-NR_2}\) and \(c_{-NR_2H^+}\). The total amount of weak-base groups is given by \(c_{-N}^0\). The value of \(c_{-N}^0\) is roughly 1.5 M for a thickness of 10 nm in the junction between the cation-exchange and anion-exchange layers. The value of \(c_{-N}^0\) is described in detail in Appendix 3.1. The total concentration of weak-base groups is related to \(c_{-NR_2}\) and \(c_{-NR_2H^+}\) by \(c_{-N}^0 = c_{-NR_2} + c_{-NR_2H^+}\). Since the flux of \(-NR_2\) and \(-NR_2H^+\) are both zero, the material balance, Equation 3.19, when written for \(-NR_2\) and \(-NR_2H^+\) becomes

\[
c_{-NR_2} = \frac{k_{-2}c_{OH^-} + k_3c_{H_2O}}{k_2c_{H_2O} + k_{-2}c_{OH^-} + k_3c_{H_2O} + k_{-3}c_{H_2O^+}} c_{-N}^0,
\]

(3.30)
and

\[
c_{-NR_2H^+} = \frac{k_2c_{H_2O} + k_{-3}c_{H_2O^+}}{k_2c_{H_2O} + k_{-2}c_{OH^-} + k_3c_{H_2O} + k_{-3}c_{H_2O^+}} c_{-N}^0.
\]

(3.31)
Equations 3.30 and 3.31 are solved along with the differential equations.

**Boundary Conditions**

The boundary conditions are chosen to approximate the bulk solutions on either side of the membrane. Since there are 10 first order ordinary differential equations, 10 boundary conditions are necessary. The boundary conditions on the left boundary are that the water-splitting reaction is equilibrated

\[
0 = k_1c_{H_2O^2} - k_{-1}c_{H_3O^+}c_{OH^-},
\]

(3.33)
that the solution is electrically neutral

\[
0 = c_{H_3O^+} - c_{OH^-} + c_{Na^+} - 2c_{SO_4^{2-}} + c_{-NR_2H^+},
\]

(3.34)
a fixed concentration of \(Na^+\)

\[
c_{Na^+} = c_{Na^+}^l,
\]

(3.35)
a fixed concentration of \(SO_4^{2-}\)

\[
c_{SO_4^{2-}} = c_{SO_4^{2-}}^l,
\]

(3.36)
and setting the electrostatic potential

\[
\Phi = 0.
\]

(3.37)
The boundary conditions on the right boundary are very similar. They are that the water-splitting reaction is equilibrated

\[
0 = k_1c_{H_2O^2} - k_{-1}c_{H_3O^+}c_{OH^-},
\]

(3.38)
that the solution is electrically neutral
\[ 0 = c_{H_3O^+} - c_{OH^-} + c_{Na^+} - 2c_{SO_4^{2-}} + c_{-NR_2H^+}, \]  
\text{(3.39)}

A fixed concentration of \(Na^+\)

\[ c_{Na^+} = c_{Na^+}^R, \]  
\text{(3.40)}

A fixed concentration of \(SO_4^{2-}\)

\[ c_{SO_4^{2-}} = c_{SO_4^{2-}}^R, \]  
\text{(3.41)}

And setting the electrostatic potential

\[ \Phi = -V. \]  
\text{(3.42)}

Salt-Solution Model-Results Summary

The governing equations, Equations 3.20-3.31, are solved subject to the boundary conditions given in Equations 3.33-3.42. Several additional parameters are used in the model. These parameters include things like diffusion coefficients, reaction rate constants, the dielectric permeability, the water content of the membrane, and so on. The value of each of these parameters was set to a value that could be reasonably expected based upon the experimental data. The values of the parameters are given in Appendix 3.1. For the case of interest, the solution on the left and right of the bipolar membrane is \(0.1 \text{ M } Na_2SO_4\). The values for the boundary conditions are then \(c_{Na^+}^L = c_{Na^+}^R = 0.2 \text{ M}\) and \(c_{SO_4^{2-}}^L = c_{SO_4^{2-}}^R = 0.1 \text{ M}\).

Additional results for an asymmetric case will be considered in a later section.

The bipolar membrane model consists of a 32-\(\mu\)m-thick stagnant diffusion layer, a 52-\(\mu\)m-thick cation-exchange layer, a 10-nm-thick catalyst layer, a 52-\(\mu\)m-thick anion-exchange layer, and a 32-\(\mu\)m-thick stagnant diffusion layer. The fixed charge density in the membrane is shown in Figure 3.5. As can be seen in Figure 3.5 the charge density in the various regions is modeled using hyperbolic tangents. This is done to allow for smooth interfaces in the membranes. The hyperbolic tangents used in these results have a characteristic length of 1.0 nm. The exact functions can be seen in Appendix 3.1.

\[ \begin{align*} 
\text{Figure 3.5.} & \text{ The charge density fixed to the membrane as a function of position for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows just the region immediately near the junction.} 
\end{align*} \]
The most important result of the bipolar membrane model is the i-v curve. The i-v curve for the bipolar membrane model is shown in Figure 3.6. The model shows excellent qualitative agreement with the experimental results of bipolar membranes published in literature, such as those of Figure 3.3. The model i-V curve displays all of the characteristic behavior of bipolar membranes: rapidly increasing current density with increases in voltage in the forward-bias direction, a limiting current region, and a breakdown of the junction in the reverse-bias direction with large biases.

It is also of interest to consider which ions are carrying the current. The fraction of the current that is being carried by hydronium and hydroxide ions as a function of current density is shown in Figure 3.7. As has been shown in the literature, the experimentally measured fraction of current that is carried by hydronium and hydroxide ions increases rapidly during breakdown of the junction. As seen in Figure 3.7, the model results agree with this experimental observation.

In order to show clearly the physical mechanisms behind the model behavior, the profiles of electrostatic potential, concentration, entropy production, and reaction rate are next shown for four different potentials. The four different potentials represent four different regions of the i-V curve. The 0 V potential shows the results at open circuit. The −0.20 V potential represents the limiting current region. The −0.65 V potential represents the region where the membrane is undergoing breakdown. Lastly, the 0.06 V potential represents the membrane under forward bias.

The entropy production is included to show where the system is behaving in an irreversible manner. By reducing the sources of entropy production, one can operate the bipolar membrane in a more energy-efficient manner. The equation solved to calculate the entropy production per volume is

\[
g_s = -\frac{1}{T} \left[ \sum_i \mu_i R_i + \sum_i N_i \frac{d\mu_i}{dx} \right].
\]

In Equation 3.43, \(g_s\) is the generation of entropy per unit volume, and \(R_i\) is the rate of generation of species \(i\) due to chemical reaction. The first summation represents the generation of entropy due to irreversible chemical reactions. The second summation represents the generation of entropy due to movement of species down gradients in electrochemical potential. It is interesting to consider which of the two sources of irreversibility is dominant.
Figure 3.6. The i-V curve for the bipolar-membrane model in a 0.1 M Na$_2$SO$_4$ solution with the parameters given in Appendix 3.1. The i-V curve displays rapidly increasing current under forward bias, a limiting current under moderate reverse bias, and breakdown under a large reverse bias.
Figure 3.7. The fraction of current due to the movement of \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) ions as a function of the current density for the parameters given in Appendix 3.1. Virtually no current is carried by \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) under forward bias and in the limiting current region. However, the fraction of current carried by \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) increases rapidly during breakdown.

Salt-Solution Model-Results at 0 V

The model results at 0 V are useful to gain an intuitive understanding of how a bipolar membrane functions. The electrostatic potential is shown in Figure 3.8 for 0 V and the parameters in Appendix 3.1. At 0 V, the electrostatic potential in the bipolar membrane varies with position at equilibrium. The variation in the electrostatic potential arises because the interfaces of the different regions show local deviations from electroneutrality. This is because the fixed charge in the membrane leads to concentration gradients of the mobile species in the membrane. The concentration of each mobile species follows a Boltzmann distribution. Since the cation-exchange layer contains the same charge density as the anion exchange layer, one could expect that the electrostatic potential in the bulk of the two layers would be the negative of one another. This does not occur because the electrolyte, \( \text{Na}_2\text{SO}_4 \), is not symmetric.

Concentration profiles are shown in Figure 3.9, Figure 3.10, and Figure 3.11. The concentration of \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) are shown in Figure 3.9. The large concentrations seen at the interface are due to the large electric field at the interface, causing increased dissociation. The concentration profiles of \( \text{Na}^+ \) and \( \text{SO}_4^{2-} \) are shown in Figure 3.10. Donnan equilibrium leads to
increased concentration of the Na$^+$ ions and decreased concentration of SO$_4^{2-}$ ions in the cation-exchange layer. Similarly, Donnan equilibrium leads to increased concentration of SO$_4^{2-}$ ion and decreased concentration of Na$^+$ in the anion-exchange layer. The concentration profiles of $-\text{NR}_2$ and $-\text{NR}_2\text{H}^+$ are shown in Figure 3.11. The majority of the weak-base groups is in the protonated form.

**Figure 3.8.** The profile of the electrostatic potential for the entire model domain at a potential of 0 V for the parameters given in Appendix 3.1.

**Figure 3.9.** The concentration profiles of H$_3$O$^+$ and OH$^-$ ions at a potential of 0 V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows just the region immediately near the junction.
Figure 3.10. The concentration profiles of $\text{Na}^+$ and $\text{SO}_4^{2-}$ ions at a potential of 0 V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows the concentration of the minority ions in the membrane.

Figure 3.11. The concentration profiles of $-\text{NR}_2$ and $-\text{NR}_2\text{H}^+$ ions near the junction at a potential of 0 V for the parameters given in Appendix 3.1.

**Salt-Solution Model-Results at -0.2 V**

When the applied potential is $-0.2$ V, the bipolar membrane is in the limiting current region of the i-V plot. In this region, further decreases in the applied potential lead to negligible
changes in the current density. The reason for this limiting current behavior can be seen by studying Figures 3.12 through 3.17.

The electrostatic potential is seen in Figure 3.12. Virtually all of the $-0.20$ V applied to the system is present at the thin junction between the cation and anion exchange layers. The concentrations of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions in Figure 3.13 have increased as compared with the case of $0.0$ V. The increase in $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions is due to the large electric field at the junction driving water dissociation. The ions created by the dissociation of water then move into the bulk of the ion exchange layers.

Figure 3.14 is the key to understanding the cause of the limiting current behavior. Figure 3.14 shows the concentrations of the $\text{Na}^+$ and $\text{SO}_4^{2-}$ ions. In the right part of Figure 3.14, the concentration of $\text{Na}^+$ in the anion exchange membrane near the junction has been driven almost to zero. The movement of the $\text{Na}^+$ in the anion-exchange membrane is primarily due to diffusion down the concentration gradient. The movement is not due to migration in the electric field. The effect of migration is negligible because the electric field in the bulk of the anion-exchange layer is small, as seen in Figure 3.12, and the concentration of $\text{Na}^+$ in the anion-exchange layer is small. Since the concentration of $\text{Na}^+$ has been driven almost to zero near the interface and the concentration of $\text{Na}^+$ is set by Donnan equilibrium at the membrane-solution interface, the concentration gradient of $\text{Na}^+$, and thus the flux of $\text{Na}^+$, cannot increase further. A similar situation is occurring for the $\text{SO}_4^{2-}$ ions in the cation exchange membrane. Thus the system is at a limit for the flux of $\text{Na}^+$ and $\text{SO}_4^{2-}$ ions. Since $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions are not at a large concentration, the contribution of these ions to the overall current density is negligible, as seen in Figure 3.7. Therefore, the system is at a limiting current.

The entropy production can be seen in Figure 3.16. The majority of irreversible behavior in the system is due to mass transfer in the anion-exchange membrane, not due to the water dissociation reaction. The reason that the contribution to mass transfer is in the anion exchange membrane is because the $\text{Na}^+$ ions have a much larger concentration gradient in the anion exchange membrane than the $\text{SO}_4^{2-}$ ions do in the cation exchange membrane. In Figure 3.18, most of the water-dissociation reaction is occurring via the uncatalyzed mechanism given by Equation 3.9, rather than by the catalyzed reaction mechanism given by Equation 3.12 and Equation 3.15.
Figure 3.12. The profile of the electrostatic potential for the entire model domain at a potential of $-0.20 \text{ V}$ for the parameters given in Appendix 3.1.

Figure 3.13. The concentration profiles of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions at a potential of $-0.20 \text{ V}$ for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows just the region immediately near the junction.
**Figure 3.14.** The concentration profiles of Na\(^+\) and SO\(_4^{2-}\) ions at a potential of \(-0.20\) V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows the concentration of the minority ions in the membrane.

**Figure 3.15.** The concentration profiles of \(-NR_2\) and \(-NR_2H^+\) groups near the junction at a potential of \(-0.20\) V for the parameters given in Appendix 3.1.
Figure 3.16. The total entropy production rate is $8.79 \times 10^{-3} \frac{J}{Km^2s}$ at a potential of $-0.20 \text{ V}$ for the parameters given in Appendix 3.1. The integrated fraction of the total entropy produced is shown as a function of position. Mass transfer through the system accounts for 85.1% of the entropy production in the system. Chemical reaction accounts for 14.9% of the entropy production. The majority of the entropy production is occurring at the interface.
The total net rate of $H_3O^+$ production is $1.20 \times 10^{-2}$ mol/m^2s at a potential of $-0.20 \text{ V}$ for the parameters given in Appendix 3.1. The integrated fraction of the total $H_3O^+$ production is shown as a function of position for the two different pathways. The catalyzed reaction pathway accounts for a fraction of $2.76 \times 10^{-5}$ of the $H_3O^+$ production.

Salt-Solution Model-Results at -0.65 V

At an applied bias of $-0.65 \text{ V}$, the bipolar membrane is undergoing breakdown. As can be seen in Figure 3.6, the current density is increasing rapidly with a greater negative bias. The current is being carried predominantly by $H_3O^+$ and $OH^-$ ions, as seen in Figure 3.7.

In Figure 3.18 it is seen that virtually all of the applied bias is applied across the junction between the cation-exchange layer and the anion-exchange layer. The bias leads to a large electric field in the junction. The large electric field drives the water-splitting reaction, leading to increases in the concentration of $H_3O^+$ and $OH^-$ ions in the junction, as seen in Figure 3.19. The large electric field dissociates so much water that the $H_3O^+$ and $OH^-$ ions have significant concentrations in the ion exchange layers. In Figure 3.20, it is seen that the increase in $H_3O^+$ and $OH^-$ ions leads to decreases in the concentration of $Na^+$ and $SO_4^{2-}$ in the bipolar membrane.

In Figure 3.21 it is seen that most of the weak-base groups present in the catalyst layer are now in the $-NR_2$ form, rather than the $-NR_2H^+$ form that dominated at a bias of 0.0 V. However, Figure 3.22 shows that mass transfer is still the dominant form of entropy production in the system. Most of this entropy is being produced near the boundaries of the model. This is because the species are at different concentrations in the bulk of the stagnant diffusion layer than the concentrations set as boundary conditions. In Figure 3.23 it is seen that virtually all of
the water dissociation reaction is occurring at the interface, and it is occurring via the uncatalyzed mechanism given by Equation 3.9.

Figure 3.18. The profile of the electrostatic potential for the entire model domain at a potential of $-0.65 \text{ V}$ for the parameters given in Appendix 3.1.

Figure 3.19. The concentration profiles of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions at a potential of $-0.65 \text{ V}$ for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows just the region immediately near the junction.
Figure 3.20. The concentration profiles of Na\(^+\) and SO\(_4\)^{2−}\) ions at a potential of −0.65 V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows the concentration of the minority ions in the membrane.

Figure 3.21. The concentration profiles of −NR\(_2\) and −NR\(_2\)H\(^+\) ions near the junction at a potential of −0.65 V for the parameters given in Appendix 3.1.
Figure 3.22. The total entropy production rate is 0.602 \( \frac{J}{Km^2s} \) at a potential of \(-0.65\) V for the parameters given in Appendix 3.1. The integrated fraction of the total entropy produced is shown as a function of position. Mass transfer through the system accounts for 88.2% of the entropy production in the system. Chemical reaction accounts for 11.8% of the entropy production. The majority of the entropy production is occurring at the edges of the stagnant diffusion layers.
Figure 3.23. The total net rate of $\text{H}_3\text{O}^+$ production is $0.638 \frac{\text{mol}}{\text{m}^2\text{s}}$ at a potential of $-0.65 \text{ V}$ for the parameters given in Appendix 3.1. The integrated fraction of the total $\text{H}_3\text{O}^+$ production is shown as a function of position for the two different pathways. The catalyzed reaction pathway accounts for a fraction of $1.87 \times 10^{-7}$ of the total $\text{H}_3\text{O}^+$ production.

Salt-Solution Model-Results at 0.06 V

When the bipolar membrane is under a bias of 0.06 V, the membrane is in forward bias. As seen in Figure 3.6, the current density increases rapidly with increasing positive bias. The current density is being carried by the $\text{Na}^+$ and $\text{SO}_4^{2-}$ ions, as seen in Figure 3.7. Unlike in the case of reverse bias, Figure 3.24 shows that while some of the applied bias goes to changing the difference in voltage across the junction between the cation-exchange layer and the anion-exchange layer, a significant portion of it is applied across the bulk of the layers.

In Figure 3.25, the concentration of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions are quite small. This is especially true when the concentrations are compared to the concentration of $\text{Na}^+$ and $\text{SO}_4^{2-}$ ions in Figure 3.26. The plot on the right in Figure 3.26 shows that just as in the case of $-0.20 \text{ V}$ bias, the coions are diffusing down a concentration gradient. However, a limiting current is not reached because, rather than the concentration of the ions being depleted near the junction, the concentration of the ions is being augmented near the junction.

The net rate of water dissociation is virtually zero. The irreversibility in the system is predominantly due to mass transfer through the membranes, seen in Figure 3.28.
Figure 3.24. The profile of the electrostatic potential for the entire model domain at a potential of 0.06 V for the parameters given in Appendix 3.1.

Figure 3.25. The concentration profiles of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions at a potential of 0.06 V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows just the region immediately near the junction.
**Figure 3.26.** The concentration profiles of Na\(^+\) and SO\(_4\)\(^{2-}\) ions at a potential of 0.06 V for the parameters given in Appendix 3.1. The left side shows the entire model domain including the bipolar membrane and the adjacent stagnant diffusion layers. The right side shows the concentration of the minority ions in the membrane.

**Figure 3.27.** The concentration profiles of R\(_3\)N and R\(_3\)NH\(^+\) ions near the junction at a potential of 0.06 V for the parameters given in Appendix 3.1.
The total entropy production rate is $1.78 \times 10^{-2} \frac{J}{Km^2s}$ at a potential of 0.06 V for the parameters given in Appendix 3.1. The integrated fraction of the total entropy produced is shown as a function of position. Chemical reaction accounts for a fraction of $8.48 \times 10^{-9}$ of the total entropy production. The majority of the entropy production is occurring at the edges of the stagnant diffusion layers.

**Effect of the Catalyst**

Catalyst layers are often added between the cation-exchange layer and the anion-exchange layer of a bipolar membrane.\(^2,5\) The catalyst layer is added because it is believed that the addition of the catalyst layer leads to a greater rate of dissociation of water. However, published experimental results are not consistent, with authors trying various catalysts with various outcomes.\(^2,5\) The mechanism for catalytic water dissociation is believed to follow a scheme like that of Equation 3.12 and Equation 3.15. The mechanism has been used to explain the greater water dissociation seen at the interface of an anion-exchange membrane with solution than the water dissociation seen at the interface of a cation-exchange membrane with solution.\(^4\) Contrary to initial expectations, the model predicts that the effect of the catalyst is negligible, as seen in Figure 3.23. It will be shown that the catalyst layer has a negligible effect on the behavior of the bipolar membrane because of the effect of the electric field upon the water dissociation reactions. The electric field impacts the uncatalyzed water dissociation reaction differently from the catalyzed water dissociation reaction. The reactions are given by Equation 3.9, Equation 3.12, and Equation 3.15.

At zero applied electric field, water dissociation via the catalytic route is faster than water dissociation via the noncatalytic route. At zero applied electric field, the parameters in Appendix 3.1 yield
\begin{align}
  k_1 &= 3.67 \times 10^{-10} \frac{\text{m}^3}{\text{mol} \cdot \text{s}}, \\
  k_2 &= 3.02 \times 10^1 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}, \\
  k_3 &= 7.04 \times 10^{-5} \frac{\text{m}^3}{\text{mol} \cdot \text{s}}.
\end{align}

Taking the concentration of water to be \(c_{\text{H}_2\text{O}} = 19.37 \text{ M}\) in the membrane, the rate of water dissociation expected by the uncatalyzed route is

\[k_1 c_{\text{H}_2\text{O}}^2 = 0.138 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}.\]  

This can be compared to the maximum rate of water dissociation via the catalytic mechanism. The total concentration of weak-base catalytic centers will be taken as \(c_{-\text{NR}_2} + c_{-\text{NR}_2\text{H}^+} = 1.5 \text{ M}\). At steady state, the rate of the reaction given by Equation 3.12 must equal the rate of reaction given by Equation 3.15. If only the dissociation reactions are occurring, then \(c_{-\text{NR}_2} = 3.50 \times 10^{-6} \text{ M}\). The rate of water dissociation via the catalytic route is then

\[k_2 c_{\text{H}_2\text{O}} c_{-\text{NR}_2} = k_3 c_{\text{H}_2\text{O}} c_{-\text{NR}_2\text{H}^+} = 2.04 \times 10^3 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}.\]  

At zero electric field, the water dissociation via the catalytic route can be over \(10^4\) times larger than water dissociation via the uncatalyzed route.

A macroscopic electric field affects the rate of water dissociation via the catalyzed route and the uncatalyzed route differently. The macroscopic electric field increases the rate constants \(k_1\) and \(k_2\) by the same factor. However, the macroscopic electric field will not increase rate constant \(k_3\). This means that, at a large enough electric field, the rate of water dissociation via the catalytic mechanism will be limited by the rate of the reaction given by Equation 3.15. Using the values of \(c_{-\text{NR}_2} + c_{-\text{NR}_2\text{H}^+} = 1.5 \text{ M}\) and \(c_{\text{H}_2\text{O}} = 19.37 \text{ M}\), the maximum rate that the water dissociation reaction can occur via the catalytic route is then

\[k_3 c_{\text{H}_2\text{O}} (c_{-\text{NR}_2} + c_{-\text{NR}_2\text{H}^+}) = 2.04 \times 10^3 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}.\]  

By comparing Equation 3.48 to Equation 3.49, one sees that the rate of water dissociation via the catalytic mechanism at zero electric field is virtually identical to the rate of water dissociation via the catalytic mechanism with a nonzero electric field.

The maximum rate of water dissociation via the uncatalyzed route and via the catalyzed route is shown in Figure 2.39. The reaction rate of the catalyzed route and uncatalyzed route is the same at \(0.0965 \frac{\text{V}}{\text{nm}}\). For electric fields less than \(0.0965 \frac{\text{V}}{\text{nm}}\), the catalyzed reaction route has a larger reaction rate. For electric fields greater than \(0.0965 \frac{\text{V}}{\text{nm}}\), the uncatalyzed reaction route has a larger reaction rate. The absolute value of the electric field in the junction of the bipolar membrane at \(-0.65 \text{ V}\) is about \(0.3 \frac{\text{V}}{\text{nm}}\). At this value of the electric field, the uncatalyzed mechanism is \(10^9\) times as large as the uncatalyzed mechanism.
Figure 3.29. The logarithm (base ten) of the maximum reaction rate as a function of the macroscopic electric field for the uncatalyzed reaction route and the catalyzed reaction route. The reaction rate of the catalyzed route and the uncatalyzed route is the same at 0.0965 V/nm.

The rate of $\text{H}_3\text{O}^+$ production in the bipolar membrane is related to the maximum electric field in the junction of the bipolar membrane. The relation can be seen in Figure 3.30. The relation is expected because the degree of dissociation of the water molecules is determined by the strength of the electric field.
Figure 3.30. The logarithm (base ten) of $\text{H}_3\text{O}^+$ production in the membrane as a function of the logarithm (base ten) of the absolute value of the maximum electric field in the junction for the parameters given in Appendix 3.1.

**Acid-Base-Solutions Results Summary**

The bipolar membrane model was also run with an acid solution adjacent to the cation-exchange layer and a base solution adjacent to the anion-exchange layer. This choice of adjacent solutions is similar to how a bipolar membrane would be used in an electrodialysis process for the production of an acid and a base. The model is the same as the model with the 0.1 M $\text{Na}_2\text{SO}_4$ except that the boundary conditions are changed. All values in Appendix 3.1 are used in the model. The values for the boundary conditions are that $c^{\text{L}}_{\text{Na}^+} = 0.19$ M, $c^{\text{R}}_{\text{Na}^+} = 0.21$ M and $c^{\text{L}}_{\text{SO}_4^{2-}} = c^{\text{R}}_{\text{SO}_4^{2-}} = 0.1$ M. The pH of the solution adjacent to the cation-exchange layer is 2. The pH of the solution adjacent to the anion exchange layer is 12. When current is passed through the bipolar membrane in the reverse-bias direction, the bipolar membrane will dissociate water. The $\text{H}_3\text{O}^+$ product is added to the acidic solution while the $\text{OH}^-$ product is added to the basic solution.

Figure 3.31 shows the i-V curve for the case of the bipolar membrane separating an acid and a base solution. The i-V curve is similar to the i-V curve for the symmetric case; however the current density is zero at $-0.580$ V, and the potential is zero at a current density of $3.75 \text{ mA/cm}^2$. The bipolar membrane still displays rapidly increasing current under forward bias, a limiting current under moderate reverse bias, and breakdown under a large reverse bias. Besides the intercepts occurring in different places for the case of acid-base solution and the
salt solution, the curve itself is slightly different. The difference in the shape of the curve is due to the different concentrations of the various species present. For example, in the left solution, the acid solution contains less Na\(^+\) ions and more H\(_3\)O\(^+\) ions than the salt solution. The different ions have different properties including the diffusivity, making the resulting i-V curve different.

The cell potential at zero current density can be predicted using a back-of-the-envelope calculation. One starts by assuming that the H\(_3\)O\(^+\) at the left boundary is in equilibrium with the H\(_3\)O\(^+\) in the junction. This can be written as

\[ \mu_{H_3O^+}^L = \mu_{H_3O^+}^J. \] (3.50)

Equation 3.50 is a good assumption because there is a large concentration of H\(_3\)O\(^+\) in the left stagnant layer and in the cation-exchange membrane. It is also assumed that the OH\(^-\) at the right boundary is in equilibrium with the OH\(^-\) in the junction, written as

\[ \mu_{OH^-}^J = \mu_{OH^-}^R. \] (3.51)

Equation 3.51 is a good assumption because there is a large concentration of OH\(^-\) in the right stagnant layer and in the anion-exchange membrane.

Additionally, one assumes that the reaction is equilibrated in the junction. This is a good assumption because the rate constant of water recombination is very large. The result of this is that the concentrations of the reactants and products are always near the level that they would be at if the reaction were equilibrated. As has been seen, the entropy production for the chemical reaction is less than the entropy production for mass transfer. This is because the large rate constants are keeping the dissociation reaction near equilibrium. The equilibrated-reaction assumption can be written as

\[ 2\mu_{H_2O} = \mu_{H_3O^+}^J + \mu_{OH^-}^J. \] (3.52)

Equation 3.50, Equation 3.51, and Equation 3.52 combined with expressions for the electrochemical potentials, Equation 3.2, Equation 3.3, and Equation 3.4, and the equilibrium constant, Equation 3.11, yields

\[ K_1^0 = \frac{c_{H_2O^+}^L c_{OH^-}^R}{c_{H_2O}^0} \exp \left( \frac{F(\Phi^L - \Phi^R)}{RT} \right). \] (3.53)

For the case of interest, Equation 3.53 yields \( \Phi^L - \Phi^R = -0.591 \) V. This back-of-the-envelope calculation compares favorably with the \( -0.580 \) V calculated using the model.
Figure 3.31. The i-V curve for the bipolar membrane with a 0.095 M Na$_2$SO$_4$, 0.005 M H$_2$SO$_4$ solution adjacent to the cation-exchange layer and a 0.1 M Na$_2$SO$_4$, 0.01 M NaOH solution adjacent to the anion exchange layer.

**Conclusion**

The bipolar membrane exhibits three distinct regions of behavior during an i-V curve. The three different regions are seen in Figure 3.6 and in Figure 3.31. The existence of the three regions is therefore not specific to the solutions adjacent to the bipolar membrane. The three different regions are forward bias, limiting current, and breakdown.

In the forward-bias region, the current density increases rapidly with increasing bias. As can be seen in Figure 3.26, the current is being carried by the ions in the supporting electrolyte. The ions migrate into the layer where they are counterions. Once the ions reach the layer with the same charge as the ions, the concentration of ions falls. This means that the ions move by diffusion down a concentration gradient. The ions build up in concentration at the junction until the concentration gradient is large enough for the ions to diffuse out of the membrane at the necessary rate.

In the limiting current region, increasing the bias to larger negative values does not lead to an increase in the current density. The reason for this is that the current is being carried by the ions in the adjacent solutions and that the concentration of these ions has been driven to near zero near the junction. This can be seen in Figure 3.14. When the ions are coions in a layer,
the concentration of these ions is small, and the movement is mainly due to diffusion down a concentration gradient. Under the conditions of reverse bias, the coions are moving towards the junction. After the concentration of coions has been decreased to zero at the junction’s interface, the flux of ions no longer increases with increasing negative bias. This causes the limiting current behavior.

The third region is breakdown. Here the current increases rapidly with increasing negative voltage. As can be seen in Figure 3.7, the current is being carried by $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions. Under the conditions of breakdown, the electric field at the junction of the bipolar membrane has become very large, as seen in Figure 3.18. Virtually all of the applied bias has been applied across the thin junction region. This large current is driving the dissociation of water into hydronium ions and hydroxide ions. These ions increase in concentration in the membrane and carry a large fraction of the current.

The bias where breakdown occurs is determined by the bias needed to reach a large electric field at the junction. Once the electric field at the junction is large enough, the water splitting reaction produces enough hydronium and hydroxide ions to carry a significant portion of the current. The amount of bias needed to achieve this electric field is determined by the membrane parameters. The necessary bias is determined only by $\Delta_{\text{rxn}} G^0$ and $\Delta_{\text{rxn}} H^0$ through how these quantities impact the reaction equilibrium at zero electric field. The increase in dissociation due to the electric field is independent of $\Delta_{\text{rxn}} G^0$ and $\Delta_{\text{rxn}} H^0$.

The effect of the catalyst is negligible. This is seen in Figure 3.17 and Figure 3.23. The effect of the catalyst is negligible because the electric field does not increase the reaction rate of the reaction in Equation 3.15. The rate that the catalyst can dissociate water therefore becomes limited by the reaction in Equation 3.15.

The main effect of changing the solutions adjacent to the bipolar membrane is to change the origin of the i-V curve. This can be seen by comparing Figure 3.6 and Figure 3.31. One can predict the potential at zero current using a back-of-the-envelope analysis. This is because the main effect of changing the adjacent solutions is to change the potential across the junctions of the bipolar membrane with the external solutions. The junction becomes chemically biased by the adjacent ions. To a first approximation, this bias simply adds to an externally imposed bias, and the i-V curve takes the same characteristics.

It is not a poor assumption to approximate the reaction as equilibrated. As can be seen by Figure 3.16 and Figure 3.22, the majority of the irreversibility in the system is due to mass transfer. At its largest, the chemical reaction accounts for less than 20% of the entropy production.

**Appendix 3.1**

There are many different physical properties appearing in the bipolar membrane model. Unfortunately, the values of each of these properties has not been experimentally measured for each bipolar membrane. In the absence of exact data, it was decided to construct the model such that the parameters were equal to that of similar systems that have been measured.

As a matter of convenience, two different reference temperatures are used in the following equations. The first reference temperature is

$$T^0 = 298.15 \, \text{K}. \quad (3.54)$$

The second reference temperature is
\[ T^* = 273.15 \text{ K.} \quad (3.55) \]

A number of different physical properties must be specified regarding the membrane. Table 3.1 contains physical parameters specifying the concentration of charge groups in the membrane, the partial molar volume of the membrane, and the thickness of the membrane interfaces.\(^5\,9\)

**Table 3.1** Constant membrane parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q^p_M )</td>
<td>1.5 \times 10^3</td>
<td>mol/m(^3)</td>
</tr>
<tr>
<td>( q^n_M )</td>
<td>1.5 \times 10^3</td>
<td>mol/m(^3)</td>
</tr>
<tr>
<td>( q^w_M )</td>
<td>1.5 \times 10^3</td>
<td>mol/m(^3)</td>
</tr>
<tr>
<td>( V^p_M )</td>
<td>0.65/( q^p_M )</td>
<td>m(^3)/mol</td>
</tr>
<tr>
<td>( V^n_M )</td>
<td>0.65/( q^n_M )</td>
<td>m(^3)/mol</td>
</tr>
<tr>
<td>( V^w_M )</td>
<td>0.65/( q^w_M )</td>
<td>m(^3)/mol</td>
</tr>
<tr>
<td>( L )</td>
<td>1.0 \times 10^{-9}</td>
<td>m</td>
</tr>
</tbody>
</table>

To specify the thickness of the various layers in the membrane and stagnant diffusion layers, six different locations are specified. These locations correspond to the left boundary, the stagnant layer/cation-exchange layer interface, the cation-exchange-layer/catalyst-layer interface, the catalyst-layer/anion-exchange-layer interface, the anion-exchange-layer/stagnant-layer interface, and the right boundary. The six locations are shown in Table 3.2.

**Table 3.2** Model interface locations.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_0 )</td>
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<tr>
<td>( x_1 )</td>
<td>32.22198 μm</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>84.44898 μm</td>
</tr>
<tr>
<td>( x_3 )</td>
<td>84.45898 μm</td>
</tr>
<tr>
<td>( x_4 )</td>
<td>136.68598 μm</td>
</tr>
<tr>
<td>( x_5 )</td>
<td>168.90780 μm</td>
</tr>
</tbody>
</table>

The concentration of charge groups in the model varies with position. The concentration of charge groups is assumed to follow a hyperbolic tangent profile. The concentration of cation-exchange groups, \( q^p \), is given by

\[ q^p = q^p_M \frac{1}{2} \left( \tanh \left( \frac{x - x_3}{L} \right) - \tanh \left( \frac{x - x_4}{L} \right) \right). \quad (3.56) \]

The concentration of anion-exchange groups, \( q^n \), is given by

\[ q^n = q^n_M \frac{1}{2} \left( \tanh \left( \frac{x - x_1}{L} \right) - \tanh \left( \frac{x - x_2}{L} \right) \right). \quad (3.57) \]

The concentration of weak-base-catalyst groups, \( c_N^0 \), is given by

\[ c_N^0 = q^w_M \frac{1}{2} \left( \tanh \left( \frac{x - x_2}{L} \right) - \tanh \left( \frac{x - x_3}{L} \right) \right). \quad (3.58) \]
The concentration of water throughout the system is referenced to the concentration of water in pure water,
\[ c_{H_2O}^0 = 55.34 \text{ M}. \] (3.59)

The concentration of water in the stagnant diffusion layers is assumed to be the same as that of pure water. The concentration of water in the membrane is calculated assuming constant partial molar volumes when mixing. The concentration of water in the system is then given by
\[ \frac{c_{H_2O}}{c_{H_2O}^0} = 1 - q^p \overline{V}_M - q^n \overline{V}_M - c_N^0 \overline{V}_M. \] (3.60)

The dielectric permittivity is expected to vary from the aqueous solution to inside the membrane. The dielectric constant of the hydrated membrane is expected to be that of a dioxane-water mixture with the same volume fraction of water. Data for the dioxane water mixture were fit to
\[ \varepsilon = \left( \varepsilon_{H_2O}^{-1} \frac{c_{H_2O}}{c_{H_2O}^0} + \varepsilon_M^{-1} \left( 1 - \frac{c_{H_2O}}{c_{H_2O}^0} \right) + \varepsilon_3^{-1} \right)^{-1}, \] (3.61)

where \( \varepsilon_{H_2O} \) is the permittivity of pure water, \( \varepsilon_M \) is the permittivity of pure dioxane, and \( \varepsilon_3 \) has been fit to data for mixtures. The permittivity of pure water was fit to data as
\[ \varepsilon_{H_2O} = \varepsilon^0 \left( 2.313 \times 10^{-2} + 9.265 \times 10^{-5} T \ln \left( \frac{T}{T_0} \right) - 3.475 \times 10^{-5} T \right)^{-1}. \] (3.62)

The permittivity of pure dioxane was found to be \( \varepsilon_M = \varepsilon^0 2.21 \). (3.63)

The fitting parameter \( \varepsilon_3 \) was found to be
\[ \varepsilon_3 = \varepsilon^0 \left( \rho_1 \left( 1 - \frac{c_{H_2O}}{c_{H_2O}^0} \right) \rho_2 \frac{c_{H_2O}}{c_{H_2O}^0} + \rho_3 \left( 1 - \frac{c_{H_2O}}{c_{H_2O}^0} \right) \frac{c_{H_2O}}{c_{H_2O}^0} \right)^{-1}, \] (3.64)

where \( \rho_1, \rho_2, \) and \( \rho_3 \) are given in Table 3.3.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_1 )</td>
<td>-0.48156</td>
</tr>
<tr>
<td>( \rho_2 )</td>
<td>-5.0266</td>
</tr>
<tr>
<td>( \rho_3 )</td>
<td>0.066044</td>
</tr>
</tbody>
</table>

The diffusion coefficients are also expected to vary with location in the model. In the solution, the diffusivities are taken to be the values of infinite dilution. In the absence of good temperature data, the diffusion coefficients are expected to follow the Stokes-Einstein relation. Data for the viscosity of water were fit to the equation
\[ \eta^{-1} = 5.63 \times 10^5 \exp \left( -\frac{1.55 \times 10^4}{RT} \right). \] (3.65)
In Equation 3.65, \( \eta \) is the viscosity of pure liquid water at 1 bar in \( \text{Pa} \cdot \text{s} \). The diffusion coefficient of \( \text{H}_3\text{O}^+ \) is\(^{14}\)

\[
D^0_{\text{H}^+} = \frac{RT}{F^2} (224.33 + 5.305(T - T^*) - 0.0113(T - T^*)^2) \times 10^{-4}. \tag{3.66}
\]

The diffusion coefficient of \( \text{OH}^- \) is\(^{14}\)

\[
D^0_{\text{OH}^-} = \frac{RT}{F^2} \left( 110.88 + 3.468(T - T^*) \right) \times 10^{-4}. \tag{3.67}
\]

The diffusion coefficient of \( \text{Na}^+ \) is\(^3\)

\[
D^0_{\text{Na}^+} = k_B T \left( 6\pi \times 1.774 \times 10^{-10} \eta \right)^{-1} + 4.648 \times 10^{-10} \left( 1 - \frac{T}{T^0} \right). \tag{3.68}
\]

The diffusion coefficient of \( \text{SO}_4^{2-} \) is\(^{13}\)

\[
D^0_{\text{SO}_4^{2-}} = k_B T \left( 6\pi \times 2.222 \times 10^{-10} \eta \right)^{-1} \tag{3.69}
\]

The diffusion coefficient of mobile species \( i \) is then expected to vary in the model as\(^{15,16}\)

\[
D_i = D^0_i \exp \left( 0.65 \left( 1 - \frac{c_{\text{H}_2\text{O}}}{c^0_{\text{H}_2\text{O}}} \right) \right). \tag{3.70}
\]

The reaction rate constants are also expected to vary with position in the model. The Bjerrum length in the model is taken to be

\[
\ell = \frac{eF}{8\pi \varepsilon_{\text{H}_2\text{O}} RT} \tag{3.71}
\]

Notice that \( \varepsilon_{\text{H}_2\text{O}} \) is used in calculating the Bjerrum length. This is done because it is expected that over the length scales that the reaction is occurring the permittivity will not be affected by the presence of the membrane. The bond length over which the reactions happen is \( a \), \( a = 0.58 \text{ nm} \).\(^{14}\) The parameter \( \alpha \) is the dimensionless \( a \), given as

\[
\alpha = \frac{a}{2\ell} \tag{3.72}
\]

The dimensionless electric field is given by \( b \). The dimensionless electric field is defined in the same way that it was defined in Chapter 2. For the reactions of interest, the dissociation produces 1-1 electrolytes. The dimensionless electric field is then

\[
b = \ell \left| \frac{eE}{k_B T} \right| \tag{3.73}
\]

Parameters for the reaction-rate constants in the absence of the electric field are given in Table 3.4. The values in Table 3.4 were calculated by fitting literature data for the reaction of water and trimethylamine.\(^{10,14,17,18,19,20,21}\)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \theta_n )</th>
<th>( A_n \left[ \text{mol} / \text{m}^3 \right] )</th>
<th>( E_n \left[ \text{J} / \text{mol} \right] )</th>
<th>( B_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>( 8.0721 \times 10^6 )</td>
<td>( 1.0908 \times 10^5 )</td>
<td>(-20.767 )</td>
</tr>
<tr>
<td>2</td>
<td>0.529</td>
<td>( A_1 / A_3 )</td>
<td>( E_1 - E_3 )</td>
<td>( B_1 - B_3 )</td>
</tr>
<tr>
<td>3</td>
<td>0.5269</td>
<td>( 6.85 \times 10^{-11} )</td>
<td>(-1.7624 \times 10^4 )</td>
<td>(-22.0 )</td>
</tr>
</tbody>
</table>
The recombination rate constants are given in terms of the data in Table 3.4. Each recombination-rate constant has been measured to be collision controlled. The recombination rate constant for the reaction given by Equation 3.9 is

\[ k_{-1}^0 = \theta_1 4\pi N_A (D_{H^+}^0 + D_{OH^-}^0) a \frac{\alpha^{-1}}{1 - \exp(-\alpha^{-1})}. \]  

The recombination rate constant for the reaction given in Equation 3.12 is

\[ k_{-2}^0 = \theta_2 4\pi N_A D_{OH}^0 a \frac{\alpha^{-1}}{1 - \exp(-\alpha^{-1})}. \]  

The recombination rate constant for the reaction given in Equation 3.15 is

\[ k_{-3}^0 = \theta_3 4\pi N_A D_{H^+}^0 a. \]  

The dissociation rate constants are given in terms of the data in Table 3.4. The dissociation rate constants were found through the use of equilibrium-constant data and the recombination-rate constant. The dissociation-rate constant for the reaction given by Equation 3.9 is

\[ k_{1}^0 = \frac{A_1}{c_{H_2O}} \left( \frac{T}{T^0} \right)^{B_1} \exp \left( \frac{-E_1}{RT} \right) \exp(-\alpha^{-1}) k_{-1}^0 \frac{k_{-1}^0}{\theta_1}. \]  

The dissociation-rate constant for the reaction given in Equation 3.12 is

\[ k_{2}^0 = \frac{\theta_3}{\theta_1} A_2 \left( \frac{T}{T^0} \right)^{B_2} \exp \left( \frac{-E_2}{RT} \right) \exp(-\alpha^{-1}) k_{-2}^0 \]  

The dissociation-rate constant for the reaction given in Equation 3.15 is

\[ k_{3}^0 = \frac{A_3}{c_{H_2O}} \left( \frac{T}{T^0} \right)^{B_3} \exp \left( \frac{-E_3}{RT} \right) \exp(-\alpha^{-1}) k_{-3}^0 \frac{k_{-3}^0}{\theta_3}. \]  

In Chapter 2, it was shown that the reaction-rate constants where two charges are dissociated or recombined are functions of the electric field. The dependence of the rate constants is taken to be the empirical fits given by Equation 2.123, Equation 2.124, and Equation 2.125. The recombination-rate constant for the reaction given by Equation 3.9 is

\[ k_{-1} = k_{-1}^0 \left( 1 + \frac{1 - \exp\left( -\frac{1}{\alpha} \right)}{2} \alpha^2 b + (4.97 \alpha) \frac{\sinh(0.0835 \alpha b)}{\cosh(0.0835 \alpha b)^2} \right). \]  

The recombination-rate constant for the reaction given in Equation 3.12 is

\[ k_{-2} = k_{-2}^0 \left( 1 + \frac{1 - \exp\left( -\frac{1}{\alpha} \right)}{2} \alpha^2 b + (4.97 \alpha) \frac{\sinh(0.0835 \alpha b)}{\cosh(0.0835 \alpha b)^2} \right). \]  

The recombination-rate constant for the reaction given in Equation 3.15 is

\[ k_{-3} = k_{-3}^0. \]  

The dissociation-rate constants include an additional parameter \( \tau \). The parameter is given by

\[ \tau = -0.128 \ln(\cosh(0.235 \alpha)) + 5.72 \alpha^2. \]  

The dissociation-rate constant for the reaction given by Equation 3.9 is

\[ k_{1}^0 = \theta_1 \frac{A_1}{c_{H_2O}} \left( \frac{T}{T^0} \right)^{B_1} \exp \left( \frac{-E_1}{RT} \right) \exp(-\alpha^{-1}) k_{-1}^0. \]  

The dissociation-rate constant for the reaction given in Equation 3.12 is

\[ k_{2}^0 = \frac{\theta_3}{\theta_1} A_2 \left( \frac{T}{T^0} \right)^{B_2} \exp \left( \frac{-E_2}{RT} \right) \exp(-\alpha^{-1}) k_{-2}^0. \]  

The dissociation-rate constant for the reaction given in Equation 3.15 is

\[ k_{3}^0 = \frac{A_3}{c_{H_2O}} \left( \frac{T}{T^0} \right)^{B_3} \exp \left( \frac{-E_3}{RT} \right) \exp(-\alpha^{-1}) k_{-3}^0 \frac{k_{-3}^0}{\theta_3}. \]
k_1 = k_1^0 \left( \sum_{m=0}^{\infty} \frac{1}{m! (m + 1)!} (2b)^m \right) \cosh(\tau b) (\cosh(\tau))^b. \quad (3.84)

The dissociation-rate constant for the reaction given in Equation 3.12 is

k_2 = k_2^0 \left( \sum_{m=0}^{\infty} \frac{1}{m! (m + 1)!} (2b)^m \right) \cosh(\tau b) (\cosh(\tau))^b. \quad (3.85)

The dissociation-rate constant for the reaction given in Equation 3.15 is

k_3 = k_3^0. \quad (3.86)

**Notation**

- $c_i$: Concentration of species $i$
- $c_i^0$: Concentration of component $i$ in pure component $i$
- $c_i^\theta$: Concentration of species $i$ in a 1 molal solution of species $i$
- $D_i$: Diffusion coefficient of species $i$
- $E$: Macroscopic electric field
- $F$: Faraday constant
- $g_s$: Entropy generation rate per volume
- $k_y^E$: Enhancement of the dissociation-rate constant of reaction $y$ due to the electric field
- $k_{-y}^E$: Enhancement of the recombination-rate constant of reaction $y$ due to the electric field
- $K_y^E$: Equilibrium constant of reaction $y$ at zero electric field
- $N_i$: Flux of species $i$
- $R_i$: Rate of generation of species $i$ due to chemical reaction
- $R$: Ideal gas constant
- $T$: Absolute temperature
- $V$: Bias
- $\varepsilon$: Dielectric permittivity
- $\Phi$: Macroscopic electrostatic potential
- $\mu_i$: Electrochemical potential of species $i$
- $\mu_i^0$: Reference state for pure component $i$
- $\mu_i^\theta$: Reference state for 1 molal solution of species $i$
Abstract


Chapter 1


Chapter 2


Chapter 3


