Deuterium Isotope Effects on the Limiting Molar Conductivities of Strong Aqueous Electrolytes from 25 °C to 325 °C at 20 MPa

by

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State of the art conductivity equipment has been used to measure deuterium isotope effects on the molar conductivity (Λ°) of strong electrolytes in the temperature range of 298 K to 598 K as a means of exploring solvation effects under hydrothermal conditions. Individual ionic contributions (λ°) were determined by extrapolation of published transference number data to elevated temperature. The temperature dependence of the Walden product ratio, (λ°η)D2O/(λ°η)H2O, indicates that there is little difference in the transport of ions between light and heavy water. Excess conductivity observed in hydrogen and deuterium compounds arising from proton hopping in hydrogen-bonded networks has been determined in the temperature range of 318 K to 598 K for the first time.
For my parents and for Abbey.
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ABBREVIATIONS

AC: Alternating Current
ASME: American Society of Mechanical Engineers
CANDU: CANadium Nuclear Deuterium
CIP: Contact Ion Pairing
FHFP: Fuoss-Hsia-Fernandez-Prini ionic conductivity model
HPLC: High Pressure Liquid Chromatography
IAPWS: International Association for the Properties of Water and Steam
MSA: Mean Spherical Approximation
NIST: National Institute of Standards and Technology
PID: Proportional Integral Derivative
RTD: Resistance Temperature Detector
SCWR: Super Critical Water-cooled Reactor
SIP: Solvent-separated Ion Pairing
SSIP: Solvent Solvent-separated Ion Pairing
TBBK: Turq-Blum-Bernard-Kunz conductivity model

NOMENCLATURE

$A$: Fitting Parameter
$A_1, A_2, A_3$: Fitting parameters
$A_s$: Surface area of the electrodes
$A_{\Lambda e}$: Arrhenius exponential factor
$A_i$: Debye-Hückel constant

$a$: Bjerrum distance

$b$: adjustable parameter

$C_i$: Capacitance at zero frequency

$C_{cell}$: Capacitance of the conductivity cell

$C_D$: Double layer capacitance

$C_p^o$: Standard partial molar heat capacity (J·mol⁻¹·K⁻¹)

c°: Hypothetical 1 mol·L⁻¹ standard state

c: Concentration (mol·L⁻¹)

d: Distance between electrodes

$E_\eta$: Faraday’s constant

$f$: Frequency (Hz)

$H^o$: Standard partial molar enthalpy (J·mol⁻¹·K⁻¹)

$I$: Applied current (A)

$I$: Ionic strength (mol·kg⁻¹ or mol·L⁻¹)

$IP$: Integrated peak ratio

$J_1$: FHFP parameter
$J_2$ : FHFP parameter

$K$: Kohlrausch’s law constant

$K_A$: Association constant

$K_{CIP}$: Association constant for contact ion pairing

$K_{T,p}$: Association constant at temperature $T$ and pressure $p$

$K_{T_r,p}$: Association constant at reference temperature $T_r$ and pressure $p_r$

$K_{SIP}$: Association constant for solvent-separated ion pairing

$K_{SSIP}$: Association constant for solvent solvent-separated ion pairing

$k_{cell}$ : Cell constant

$k_s$ : Spring constant

$m$: Molality (mol·kg$^{-1}$)

$M$: Molecular weight (g·mol$^{-1}$)

$m_W$: Slope of the Warburg line

$N$: Avagadro’s Number

$n$: Number of molecules

$p$: Pressure (MPa)

$pK_{D2O}$: Ionization constant of heavy water

$pK_w$: Ionization constant of water

$R$: Molar gas constant (J·K$^{-1}$·mol$^{-1}$)

$R_{e}$: Resistance (Ω)

$R_{ct}$ : Charge transfer resistance (Ω)

$R_s$: Solution resistance (Ω)

$R_{Walden}^{D/H}$: Walden product ratio
\( r_{\text{Stokes}} \): Stokes radius

\( S \): Onsager limiting slope

\( T \): Temperature (Kelvin)

\( \bar{r} \): Transference number at infinite dilution

\( V \): Voltage (V)

\( V^o \): Standard partial molar volume (cm\(^3\)·mol\(^{-1}\))

\( V_\phi \): Apparent molar volume (cm\(^3\)·mol\(^{-1}\))

\( w_1 \): Mass of solvent (g)

\( w_2 \): Mass of a solute (g)

\( Z_{\text{Im}} \): Imaginary component of the impedance in \( \Omega \)

\( Z_{\text{Re}} \): Real component part of the impedance in \( \Omega \)

\( z \): Absolute value of charge

**Greek Symbols:**

\( \alpha \): Degree of dissociation.

\( \alpha_w \): Fraction of pure capacitance

\( \eta \): Viscosity (Pa·s)

\( \eta_{\text{D}_2\text{O}} \): Viscosity of heavy water (Pa·s)

\( \eta_w \): Viscosity of water (Pa·s)

\( \varepsilon_r \): Dielectric constant

\( \varepsilon_w \): Dielectric constant of water

\( \gamma_\pm \): Mean activity coefficient of the electrolyte
κ: Specific conductivity (S·cm⁻¹)
Λ: Molar conductivity (S·cm²·mol⁻¹)
Λ°: Limiting molar conductivity (S·cm²·mol⁻¹)
Λ°∞: Limiting molar conductivity at zero density
Λ°r: Reduced equivalent conductivity
Λ°exp: Experimental equivalent conductivity (S·cm²·mol⁻¹)
λ°: Limiting ionic conductivity (S·cm²·mol⁻¹)
λ°E: Excess limiting ionic conductivity (S·cm²·mol⁻¹)
μ: Reduced mass (g)
v: Stoichiometric number
ω: Angular frequency (Hz)
ωo: Angular frequency of a harmonic oscillator (Hz)
ρsoln: Density of the solution (kg·m⁻³)
ρD²O: Density of heavy water (kg·m⁻³)
ρr(elect): Density at zero conductivity
ρr(elect): Reduced density
ρw: Density of water (kg·m⁻³)
Chapter 1 Introduction

1.1 General Overview

The demand for high temperature and pressure solution chemistry, also known as hydrothermal chemistry, has arisen from industrial and geochemical interest in modelling properties of water under extreme temperature and pressure. Properties such as mass-transport, corrosion and redox mechanisms are all targets of such research. (Weingartner and Franck, 2005). In addition, hydrothermal solution chemistry is fascinating on a scientific level, as the physical properties of water vary greatly from ambient to supercritical conditions resulting in significant differences in the behaviour of aquatic species over this range of conditions. Modelling of hydrothermal systems has become quite sophisticated, but the accuracy of these models is dependent on high quality experimental research.

This research is scientifically intriguing, and in the case of our research group is supported by funding provided by partners in the Canadian nuclear industry. To extend the uptime and lifetime of nuclear reactors, the industry requires precise data to model the behaviour of ions at reactor temperatures. The focus of this study is to look at the diffusion of ions, which will be used by industrial researchers to interpret and model corrosion processes and radiolysis effects within reactor systems.

The current reactor design in Canada uses heavy water in the primary circuit through the core, yet the industry relies on light water data as heavy water measurements are lacking at reactor conditions. A method to predict the behaviour of ions in heavy
water based on light water data could significantly improve the accuracy of industrial models. Measurements of the same solute in light and heavy water under the same conditions will also provide insights into the differences in ionic solvation between the solvents as a function of the temperature.

Proposed next generation nuclear reactors will have greatly increased operating conditions, from $T = 523\, \text{K}$ to $573\, \text{K}$ in modern reactors to $T = 573\, \text{K}$ to $923\, \text{K}$. This temperature range spans the critical point of water. The behaviour of ions in the reactor core under these conditions is very interesting but could cause potentially damaging effects, such as erosion, deposition and radiolysis. This behaviour requires a full investigation prior to these designs being commissioned.

The behaviour of ions in light water is well documented, although measurements around the critical point of water are sparse. Further studies of ions in the intermediate range through the critical point of water ($\sim 573\, \text{K}$ to $723\, \text{K}$) are required for proper understanding of changes in behaviour that will accompany the changes in physical properties at high temperatures and pressures. Ions that are a by-product of nuclear reactors (such as $\text{Cs}^+$, $\Gamma$, $\text{Sr}^{2+}$, etc.) are of particular interest to the industry, as their presence is unavoidable in the reactor.

This thesis will present conductivity studies on several solutions of simple ions, hydrochloric acid, potassium and sodium hydroxide in light and heavy water from $T = 298\, \text{K}$ to $588\, \text{K}$. Limiting molar and ionic conductivities have been measured for a number of species in $\text{D}_2\text{O}$ for the very first time above $338\, \text{K}$. These values offer insight into relative hydration of ionic species up to hydrothermal conditions. In addition, a method of extrapolating transference numbers in both light and heavy water from
ambient to hydrothermal conditions has been refined and tested against literature values.
The excess conductivity arising from proton hopping and the solvent isotope effect on proton hopping has been determined for the first time above 348 K.

1.2 Experimental Rationale

1.2.1 CANDU Nuclear Reactor Design

The current fleet of nuclear reactors in Canada is based on the CANDU (CANadian Deuterium Uranium) design shown in Figure 1.1. This design differs from others used around the world in that it uses \( \text{D}_2\text{O} \) rather than \( \text{H}_2\text{O} \) in its primary circuit (the circuit which enters the core). The rationale behind this design is that the low cross section for neutron absorption by \( \text{D}_2\text{O} \) allows non-enriched uranium to be used as fuel for the reactor (McFarland *et al.*, 2001).

The design has two circuits for power generation. The pressurized (10 MPa) primary circuit passes through the core, where the heavy water is heated from 523 to 573 K (250 °C to 300 °C), then through a boiler which acts as a heat exchanger before cycling back through the core. In the boiler, light water is converted to steam, which travels through the secondary circuit powering the turbine which generates the electricity. The steam continues onward to a condenser which cools it, returning it to a liquid state which is pumped back to the boiler unit.

These reactors are multi-billion dollar capital investments, whose lifetimes have been extended past their projected design date through a combination of upgrades, component replacements, and tightly controlled reactor chemistry. One of the chief concerns is the thinning of feeder tubes at the high temperature end of the reactor core.
caused by the rapid flow of D\textsubscript{2}O and dissolved ions within the circuit. To minimize the feeder tube thinning, quantifying the small differences between the chemistry of ions in high temperature light and heavy water is of great interest for our industrial funders. The differences caused by solvent isotope effects (S.I.E.’s) between light and heavy water have been studied at low temperatures, and are used currently by the industry to determine the SIE at high temperatures.

In the recent past, our group has begun basic scientific research to examine deuterium solvent isotope effects at elevated temperatures. This research was spurred largely by the need to reduce the dissolution of a passivating layer of magnetite (Fe\textsubscript{3}O\textsubscript{4}) coating the inner surface of the inlet and outlet feeder tubes of the primary circuit. Oxide dissolution is highly dependent on the chemical and physical conditions in the primary circuit. Studies of magnetite solubility in light water (Sweeton and Baes, 1970, Tremaine and LeBlanc, 1980) have shown that the solubility of magnetite is highly pH dependent. In principle, optimizing the pH of the primary circuit can greatly slow the dissolution of the magnetite layer. Much of our research group’s focus is on determining the difference in pK\textsubscript{a} for oxyacids in light and heavy water at reactor conditions so that models can be developed to optimize the pH correction required to maximize the lifetime at the feeder tubes. (Bulemela and Tremaine, 2009, Erickson \textit{et al.}, 2011)

While conducting this research, it became apparent that the unique advantages of our conductivity equipment (which will be discussed in Sections 2.3 and 2.4) would allow us to use D\textsubscript{2}O as a probe for ionic solvation at elevated temperatures and pressures. By looking at the relative changes in transport properties between light and heavy water from ambient to reactor conditions in, one can determine the relative ionic solvation
changes. As the pH of the circuit is tightly controlled, there is particular interest in the transport of protons and hydroxide ions, which is greatly affected by changes in the local solvent environment (see Section 1.5.6)

### 1.2.2 SCWR Nuclear Reactor Design

In the year 2000, the Generation IV International Forum was convened to discuss and explore technology and processes which could be utilized for future energy systems. Currently consisting of thirteen different countries, the group has explored several different systems for sustainable energy creation and has selected six concepts that they deemed most worthy of further study.

Of the six concepts put forward for further consideration as Generation IV nuclear reactors, Canada selected the SCWR (Super Critical Water-cooled Reactor) as one of the two designs to explore. A partial schematic diagram for the reactor core and primary circuit is shown in Figure 1.2. There are two major differences between this concept and the CANDU reactors in service today. Firstly there is a single circuit which carries $\mathrm{H}_2\mathrm{O}$ from the core through the turbine and back; secondly the temperature gradient through the core is from 588 K to 898 K, (315°C to 625°C) at a pressure of 25MPa.

This design concept has some glaring challenges that need to be addressed prior to its implementation. As it is a single circuit with a very large temperature gradient, the solubility of metal ions and fission products is very likely going to be a major concern. The temperature range through the core passes over the critical point of water ($T_c = 647.10 \text{ K}; p_c = 22.06 \text{ MPa}$), where the solvent will undergo a transition from a liquid-like
fluid to a dense gas. Experience with supercritical thermal power stations suggest that this will cause deposition of salts and metal oxides to occur in the range 673-723K.

Understanding the complex chemistry within the primary circuit will be a major hurdle for the designers. Metal species such as \( \text{Cr}^{3+} \), \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Ni}^{2+} \) and \( \text{ZrO}^{2+} \) from dissolution of reactor components as well as trace ions arising from alloying metals, condenser leaks and fission products such as \( \text{I}^{129} \), \( \text{Cs}^{135} \), \( \text{Cs}^{137} \) and \( \text{Sr}^{90} \). These elements are unavoidable and may lead to increased corrosion product deposition on fuel bundles, resulting in reduced power generation or fuel (Guzonas et al., 2009.) The deposits may also lead to ‘hideout’ reactions, which are caused when species are concentrated in microscopic crevices, creating local ‘hot spots’ which can cause significant damage to reactor components. A further concern is an increase in deposition of radioactive species, which would present its own significant worker safety challenge.

The other major concern going forward for the SCWR concept is radiolysis effects under reactor conditions. The redox chemistry in the current fleet of CANDU reactors is controlled by addition of an excess of hydrogen into the reactor circuit, but it is not known whether this strategy will be as effective for the SCWR (Guzonas et al., 2009). The goal is to limit the formation of oxidizing products from water, which will in turn limit the corrosion product generation and deposition within the circuit. In order to accurately predict the radiolysis reactions, industrial scientists plan to use computer simulation, however they require experimental data to build and test these systems.

The super-critical region (\( \sim 300^\circ\text{C} \) to \( 450^\circ\text{C} \)) is largely bereft of measurements in regards to transport properties and ion association. This is largely due to the heavy toll that experimental work around the critical point takes on analytical instruments. For this
reason, basic frontier research on ion association and transport properties for simple ions, acids and bases under hydrothermal conditions is of great interest to our group.

1.3 Physical Properties of H₂O and D₂O

1.3.1 Standard Formulations

Standard formulations for the PVT properties of water have been developed by the International Association for the Properties of Water and Steam (IAPWS) to provide extremely accurate calculations of physical and transport properties up to hydrothermal conditions. These formulations have been programmed into a standard database which can be used to calculate PVT properties over a range of conditions (ASME and IAPWS Formulation for Water and Steam, v. 10.0). The most recent version, from 1995, uses Helmholtz free energy to determine the various properties (Wagner and Prüß, 2002). In addition, a supplementary database called REFPROP (REFPROP: Equations of state for pure and binary liquids, v. 8.0) has incorporated equations of state for D₂O from Hill et al. (1982) and Kestin and Sengers (1986).

These formulations can be used to determine solvent properties as a function of temperature and pressure. In this thesis, the densities of H₂O and D₂O were calculated by the fundamental equations of state provided by Wagner and Prüß (2002) and Hill et al. (1982) respectively. The viscosity of both solvents was calculated from the equations provided by Kestin and Sengers (1986.) The dielectric constant of water was determined from equations provided by Fernández et al. (1995). For the dielectric constant in D₂O we employed the method of Trevani et al. (2007) which uses the equations reported by Uematsu and Franck (1980). The ionization constant of water has been reported as a
function of temperature and density by Marshall and Franck (1981), while the self-ionization constant for D₂O, pK_{D2O} has been reported by Mesmer and Herting (1978) up to 573 K. These formulations will be utilized to determine the solvent properties over experimental conditions.

1.3.2 Solvent Comparison

The most scientifically intriguing aspect of using both light and heavy water as a solvent is that the physical properties of each do not change to the same degree from ambient to supercritical conditions. These properties include density, \( \rho \), viscosity, \( \eta \), dielectric constant, \( \varepsilon \), and the self-ionization constant, \( pK_w \). At ambient conditions, H₂O has a lower density, viscosity, and dielectric constant and a greater degree of dissociation than D₂O under the same conditions. At ambient conditions, the hydrogen bonding in H₂O and D₂O is strong, resulting in a tetrahedral orientation of molecules within the build solvent and an average coordination number of 4 (Nakahara, 2004). The differences in physical properties arise from the differences in mass between hydrogen and deuterium. In addition, the differences in the properties of these solvents at elevated temperatures and pressures are not consistent with what is observed at ambient temperatures. D₂O, the heavier and more strongly hydrogen bonded solvent molecule at ambient conditions would be expected to have a higher critical point than H₂O, however its critical point is actually lower than that of water (D₂O: \( T_c = 643.89 \) K; \( p_c = 21.67 \) MPa; H₂O: \( T_c = 647.10 \) K; \( p_c = 22.06 \) MPa). The densities of the solvents approach parity at hydrothermal conditions which indicates that the relative strength of the hydrogen bonds in D₂O decreases compared to those in H₂O at elevated temperatures.
By representing the O-H and O-D bonds as harmonic oscillators (McQuarrie and Simon, 1997), the bond energy difference is proportional to the reduced mass of the system. The reduced mass, $\mu$, is given by:

$$\mu = \frac{w_a \cdot w_b}{w_a + w_b}$$  \hspace{1cm} (1.1)

where $w_a$ and $w_b$ are the masses of each atom in the bond. The reduced mass is used to find the angular frequency, $\omega_M$, of a harmonic oscillator using Hooke’s law:

$$\omega_M = \frac{k_s}{\mu}$$  \hspace{1cm} (1.2)

here $k_s$ is a spring constant. The mass of a deuterium atom is twice that of hydrogen, thus the reduced mass for O-D is nearly twice that of O-H, leading to a greatly reduced harmonic oscillation of $D_2O$ versus $H_2O$. The energy levels of a harmonic oscillator are defined by:

$$E_v = \sqrt{\frac{k_s}{\mu} \left( v + \frac{1}{2} \right)}$$  \hspace{1cm} (1.3)

where $v$ is the vibrational energy level. The zero point energy $E_0$ is significantly lower for $D_2O$ than $H_2O$, resulting in stronger inter-molecular bonds. This difference in bond strength is the cause of the disparity between the physical properties of light and heavy water at ambient conditions.
1.4 Solution Conductivity

1.4.1- Solution Resistance and Conductivity

It is important to distinguish between conductivity of ionic solutions and that of metallic conductors. The movement of electrons in a metallic conductor is a quantum movement of charge in a conduction band, whereas the conductance in electrolyte solutions is based on the movement of ions within a solvent, whose motion is governed by classical laws of physics. In solvents such as H$_2$O and D$_2$O, the contribution of hydrogen-bonding changes with temperature and pressure, altering the solvent structure and affecting the ionic mobility (Kell, 1972; Ueno et al., 1990). As a result, conductance measurements offer an insight into the transport of ions in solution, which can be used to determine physical properties of the solvated ions. Determination of conductance parameters allows for the understanding of the interaction between ions and the solvent, ions and other ions and the solvent with the solvent.

Ohm’s law describes the movement of a charge through an electric circuit:

$$ V = I \cdot R_c, $$

where $V$ is the measured voltage, $R_c$ is the resistance (in ohms) and $I$ is the applied current. For measurements of charge movement in solution, the specific conductivity, $\kappa$ (S·cm$^{-1}$) is determined by the following:

$$ \kappa = \frac{d}{A_s \cdot R_c} = k_{cell} \cdot \frac{1}{R_c}, $$

here $d$ is the distance between electrodes, $A_s$ is the surface area of the electrodes and $R$ is the solution resistance. For conductivity cells, the ratio of $d/A$ is the cell constant, $k_{cell}$, and is determined using by measuring the conductivity of a standard solution before...
experimental data are collected. The method for determination will be outlined in Chapter 2.

The specific conductivity, $\kappa$, as the name implies is specific to the solution concentration as well as the ionic charge. Molar conductivity, $\Lambda$ is a more meaningful metric. The expression for molar conductivity of a 1:1 electrolyte is:

$$\Lambda = \frac{\kappa}{c},$$  \hspace{1cm} \text{(1.6)}

Here, $c$ is the concentration of the electrolyte in mol·L$^{-1}$. The conductivity of a solution varies as a function of temperature. Kohlrausch’s law (Atkins and de Paula, 2010) shows that the limiting behaviour for strong electrolytes in dilute solutions varies with the square root of the concentration,

$$\Lambda = \Lambda^0 - K \cdot c^{1/2},$$  \hspace{1cm} \text{(1.7)}

In this case, $K$ is a constant that depends on the stoichiometry of the electrolyte and $\Lambda^0$ is the molar conductivity at zero concentration, the limiting molar conductivity.

Furthermore, the limiting molar conductivity is a sum of the limiting ionic contributions of each ion ($\lambda^0$):

$$\Lambda^0 = \nu_+ \lambda^0_{M^+} + \nu_- \lambda^0_{X^-},$$  \hspace{1cm} \text{(1.8)}

where $\nu$ is the stoichiometric number of each ion per mole of electrolyte.

Values for the limiting ionic conductivity can be determined from the limiting molar conductivity using transference numbers at infinite dilution $t^0$. Transference numbers represent the proportion of total charge each ion carries in solution:

$$\lambda^0 = t^0 \cdot \Lambda^0,$$  \hspace{1cm} \text{(1.9)}
Transference numbers for ions in a single solution sum to a value of 1. For binary solutions, the relationship between transport numbers for the cation and anion is:

\[ t_c^o = 1 - t_a^o, \]  

(1.10)

The determination of transference numbers in high temperature water will be further discussed in Section 1.4.4.

### 1.4.2- Impedance Measurements

Solution conductivity cells consist of two oppositely charged electrodes arranged in such a manner than the solution sits or flows between them, depending upon the design. Alternating current is directed between the plates to induce the ionic movement within solution, causing a current to flow through the circuit. This current is measured to determine the solution conductivity. Because the voltage (\(V\)) and applied current (\(I\)) are out of phase, the cell behaves like an impedance circuit rather than a simple resistor.

Completing measurements using an AC conductance cell yields a series of values for the real and imaginary impedance, \(Z_{Re}(\omega)\) and \(Z_{Im}(\omega)\) as a function of the applied frequency, \(\omega\):

\[ Z(\omega) = Z_{Re}(\omega) - jZ_{Im}(\omega), \]  

(1.11)

where \(Z\) is the complex impedance, and \(Z_{Re}\) and \(Z_{Im}\) are the real and imaginary components of the impedance.

To represent the contribution of different electrochemical and transport processes to the impedance of the cell, an equivalent circuit model is often used. This model is comprised of 6 different processes (Park et al., 2006) which are shown in Figure 1.3. As illustrated in the figure, \(C_{cell}\) is the capacitance across the boundaries of the cell, while
\( C_D \) is the capacitance of the double layer of charge built up upon the electrodes. The resistivity of the solution \( R_s \) is value that we wish to determine experimentally. The resistivity of charge transfer, \( R_{ct} \) is caused by redox type reactions that occur near the electrodes. The final two contributions are from \( \alpha_w \), the fraction of pure capacitance of the electrodes, and \( C_l \), the capacitance at zero frequency. These terms make up the Warburg impedance, which is the limit of ionic diffusion.

To illustrate the contribution of each of these processes as well as determine the solution resistivity, a Nyquist plot of \( Z_{Re} \) vs. \( Z_{Im} \) is shown in Figure 1.4. The Nyquist plot for an AC conductivity measurement consists of a semicircular shape in the high frequency region and linear increase at the low frequency region. The low frequency region is dominated by the Warburg impedance and will cross the x-axis at approximately \( R_s + R_{ct} \). Hnedkovsky et al. (2005) showed that the contribution due to \( R_{ct} \) is relatively small and consistent, thus by extrapolating the Warburg line to \( Z_{Im} = 0 \), the solution resistivity can be found.

1.4.3 The Hnedkovsky Extrapolation

As shown in Figure 1.4, Warburg impedance dominates in the low frequency range, but at higher frequencies it is greatly diminished which allows for determination of the solution resistance directly. The method reported by Hnedkovsky et al. (2005) extrapolates to infinite frequency to find the value of \( R_s \):

\[
Z_{Re} = R_s + \frac{b}{f^{\alpha_w}}, \quad (1.12)
\]

where \( b \) is an adjustable parameter; \( f \) is the frequency; and \( \alpha_w \) is:
\[ \alpha_w = \frac{2}{\pi} \tan^{-1} m_w. \]  

(1.13)

Here \( m_w \) is the slope of the Warburg line. As \( f^w \) approaches infinity, the solution resistivity can be determined from the real portion of the impedance through plots of \( Z_{Re} \) vs \( 1/ f^w \), to yielded \( (R_s + R_{ct} \approx R_d) \)

### 1.4.4 Transference Numbers at Elevated Temperatures

Measurements by numerous authors in the past century have reported transference numbers near ambient temperatures (Longsworth, 1932, MacInnes and Longsworth, 1932, Allgood et al., 1940, Allgood and Gordon, 1942, Smith and Dismukes, 1963, 1964). For the most common 1:1 electrolytes, NaCl and KCl, the highest temperatures reported were 398 K and 388 K respectively. The highest temperature study was conducted by Smith and Dismukes (1963, 1964) who have shown that transference numbers change in a linear function with temperature, \( T \), over the known range of \( T = 288 \) K to \( T = 398 \) K:

\[
\log \left( \frac{t^o}{t^o_T} \right) \text{ vs } \frac{1000}{T}, \tag{1.14}
\]

This relationship can be used to extrapolate values of \( t^o \) from literature sources to hydrothermal conditions. Figure 1.5 (NaCl) and Figure 1.6 (KCl) are reproductions of the plots constructed by Smith and Dismukes (1963, 1964) to fit the literature values listed in the paragraph above of \( t^o \) with inverse temperature, over the range \( T = 288 \) K to 398 K for NaCl and \( T = 288 \) K to 388 K for KCl from which the equation of the line can be used to determine the change in transference with temperature up to hydrothermal conditions.
The equation to determine the transference number change with temperature takes the form:

\[ t^o = (1 + 10 \left( \frac{m_t}{T} \right)^b_t) \]

(1.15)

here \( m_t \) is the slope of the line and \( b_t \) is the intercept. The values for \( m_t \) and \( b_t \) for Figures 1.5 and 1.6 are presented in Table 1.1.

This transference number relationship was used by Marshall (1987) in the formulation of his reduced density relationship (see Section 1.5.8) which has been the standard for determination of single ion values for the past decades, meaning that the determination of single ionic conductivity has been based on the work of Smith and Dismukes (1963, 1964), which reached a temperature maximum at \( T = 398 \) K. Recently Zimmerman et al. (2012) have revisited Marshall’s model using modern conductivity measurements and have developed their own model for fitting single ion conductivity, which will be further discussed in Sections 1.5.8 and 3.3.

Measurements for transference numbers in D\(_2\)O are much rarer than in H\(_2\)O. Values have been reported at 298K for NaCl (Swain and Evans, 1966) and for KCl at 288K (Ueno et al., 1987), 298K (Nakahara et al., 1985) and 318K (Ueno et al., 1990) by researchers in Kyoto, Japan. The transference values for these ions in heavy water differ from the values reported in light water, indicating that the change in solvent structure has a slight effect on transference. Our method of extrapolating \( t^o \) for ions in D\(_2\)O to hydrothermal conditions will be explained in Section 3.3.
1.5 Conductivity Models and Ion Transport

1.5.1 Introduction

Modern conductivity equations must account for ion-ion and ion-solvent interactions. The Debye-Hückel theory was incorporated by Onsager (1927) into a model for the dependence of ionic conductivity which considers relaxation and electrophoretic effects. The base form of the equation is the same as Kohlrausch’s empirical law:

\[ \Lambda = \Lambda^0 - S \cdot c^{1/2} \]  

where \( S \) is the limiting-law slope which represented by:

\[ S = \alpha \cdot \Lambda^+ + \beta \]  

\[ \alpha = \frac{82.046 \times 10^4 \cdot z^2}{(\varepsilon \cdot T)^{3/2}} \]  

\[ \beta = \frac{8.2487 \cdot z}{\eta (\varepsilon \cdot T)^{1/2}} \]

and \( \eta \) is the viscosity of the solvent in Pa·s. The Onsager limiting slope is important for deriving ion-pair formation constants from conductivity measurements, as deviations from the line indicate ion association. The Debye-Hückel-Onsager theory (Onsager, 1927) is the basis for modern equations.

1.5.2 The FHFP Equation

The Fuoss-Hsia-Fernández-Prini conductivity model (FHFP) is an extension of the Debye-Hückel-Onsager theory (Fernández-Prini, 1969) which accounts for higher order contributions caused by short range ionic interaction. The model is rigorous but was found to only be applicable for dilute, binary, symmetrical electrolyte systems. It takes the form:
\[ \Lambda = \Lambda^o - S \cdot c^{1/2} + E \cdot c \cdot \ln c + J_1 \cdot c - J_2 \cdot c^{3/2} \]  

(1.20)

where:

\[ E = (E_1 \cdot \Lambda^o) - E_2, \]  

(1.21)

with:

\[ E_1 = \frac{(k \cdot a \cdot b)^2}{24 \cdot c} = \frac{(2.94257 \cdot 10^{12}) \cdot z^6}{(\varepsilon_w \cdot T)^{1/2}} \]  

(1.22)

\[ E_2 = \frac{k \cdot a \cdot b \cdot \beta_k}{16 \cdot c^{1/2}} = \frac{(4.33244 \cdot 10^7) \cdot z^5}{\eta_w \cdot (\varepsilon_w \cdot T)^{3/2}} \]  

(1.23)

\[ J_1 = 2 \cdot E_1 \cdot \Lambda^o \left[ \ln \left( \frac{k \cdot a}{c^{1/2}} \right) + \Delta_1 \right] + 2 \cdot E_2 \cdot \left[ \Delta_2 - \ln \left( \frac{k \cdot a}{c^{1/2}} \right) \right] \]  

(1.24)

\[ J_2 = \frac{k \cdot a \cdot b}{c^{1/2}} \left[ (4 \cdot E_1 \cdot \Lambda^o \cdot \Delta_3) + (2 \cdot E_2 \cdot \Delta_4) \right] - \Delta_5, \]  

(1.25)

\[ b \cdot a = \frac{(z \cdot e)^2}{\varepsilon_w \cdot k_B \cdot T} = \frac{(16.7099 \cdot 10^4) \cdot z^2}{\varepsilon_w \cdot T} \]  

(1.26)

\[ k = \left( \frac{4 \cdot \pi}{\varepsilon_w \cdot k_B \cdot T} \sum_i C_i \cdot z_i^2 \right)^{1/2} = \frac{50.2916 \cdot z \cdot c^{1/2}}{(\varepsilon_w \cdot T)^{1/2}} \]  

(1.27)

\[ \Delta_1 = \frac{1}{b^3} \left[ (2 \cdot b^2) + (2 \cdot b) - 1 \right] + 0.90735 \]  

(1.28)

\[ \Delta_2 = \frac{22}{3 \cdot b} + 0.01420 \]  

(1.29)

\[ \Delta_3 = \frac{0.9571}{b^3} + \frac{1.1187}{b^2} + \frac{0.1523}{b} \]  

(1.30)

\[ \Delta_4 = \frac{1}{b^3} \left[ (0.5738 \cdot b^2) + (7.0572 \cdot b) - \frac{2}{3} \right] - 0.6461 \]  

(1.31)
Here $\varepsilon_w$ is the dielectric constant of water, $\eta_w$ is the viscosity of water and $a$ is defined as the Bjerrum distance:

$$a = \frac{(16.7099 \cdot 10^4) \cdot z^2}{b \cdot \varepsilon_w \cdot T}$$  \hspace{1cm} (1.33)

and $b = 2$. The terms $J_1$ and $J_2$ are associated with the electrophoretic effect and the relaxation of the solvent following the passing of ions through the local environment.

### 1.5.3 The TBBK Equation

A more rigorous treatment, known as the Turq-Blum-Bernard-Kunz (TBBK) model (Turq et al., 1995) builds upon the conductivity theory developed by Fuoss and Onsager (1957) by adding expressions for the structural properties and equilibrium in the electrolyte solution which are based upon Mean Sphere Approximation theory. This means electrophoretic and relaxation effects on conductivity measurements are treated separately using the MSA theory, as opposed to the FHFP theory which treats them together. The TBBK is more versatile, and is applicable for asymmetric electrolytes and a wide range of concentrations (Turq et al., 1995). The TBBK model is a significantly more complex treatment than other models for determining limiting conductivity.

A comparison of the TBBK equation with the FHFP model was conducted by Bianchi et al. (2000) and again by Sharygin et al. (2001), both of which indicated that the FHFP equation yielded more accurate results for symmetrical electrolytes in dilute solutions.
1.5.4 Ion Pairing

Strong electrolytes fully dissociate at low temperatures, but as discussed in Section 1.2.2 strongly dissociated ions are known to ion-pair at elevated temperatures and pressures. The work of Eigen and Tamm, (1962; 1962) indicates that ion-pairing occurs in three distinct types based on the nature of the hydration sphere that surrounds and separates them, as illustrated in Figure 1.7.

Figure 1.7a depicts solvent-solvent separated ion pairing (SSIP). This, the first stage of ion pairing, occurs when the solvation shells of both the anion and cation remain intact. Figure 1.7b depicts solvent separated ion pairing (SIP) with two pairing ions sharing a solvation sphere. Contact ion pairing (CIP) is represented in Figure 1.7c, where the ions are in direct contact. The pairing proceeds in the order: solvent-solvent separated ion pairs, to solvent separated ions pairs to contact ion pairs as the concentration increases. The equilibria between these types of ion pairing and unpaired ions are represented as:

\[
M^+ + X^- \rightleftharpoons K_{SSIP} \rightarrow M^+(H_2O)_2X^- \rightleftharpoons K_{SIP} \rightarrow M^+(H_2O)X^- \rightleftharpoons K_{CIP} \rightarrow MX. \quad (1.34a)
\]

The overall association constant \( K_A \) can be written as a function of each individual ion pairing constant such that (Marcus and Hefter, 2006):

\[
K_A = K_{SSIP} + K_{SSIP} \cdot K_{SIP} + K_{SSIP} \cdot K_{SIP} \cdot K_{CIP} \quad (1.34b)
\]

Conductivity measurements are particularly useful in determining the ion pairing of an electrolyte solution. Arrhenius’ original experiments that led to ion pairing theory were performed using (crude) conductance techniques. In general, as ion pairing occurs, the limiting conductance of the electrolyte solution will decrease as the fraction of free ions decreases.
The determination of the association constant of the system, $K_A$, requires the
determination of the conductivity of the associated solutions and the individual ions. The
association constant of the system is given by the expression:

$$K_A = (1 - \alpha)c^o / (\alpha^2 \gamma^2_\pm c^2),$$  \hspace{1cm} (1.35)

here $c$ is the concentration; $\alpha$ is the degree of ionization such that:

$$M^+_{aq} + X^-_{aq} \rightleftharpoons M X^0_{aq};$$

$$\alpha c \quad \alpha c \quad (1-\alpha)c,$$  \hspace{1cm} (1.36)

and $\gamma_\pm$ is the mean activity coefficient, which may be calculated using the extended
Debye-Hückel equation:

$$\log \gamma_{c,\pm} = -\frac{A_f (\alpha c)^{1/2}}{1 + \frac{50.2916 z^2 a (\alpha c)^{1/2}}{(\varepsilon T)^{1/2}}},$$  \hspace{1cm} (1.37)

where $A_f$ is a Debye-Hückel constant, $z$ is absolute value of charge and $\varepsilon$ is the dielectric
constant of the solvent. The degree of dissociation, $\alpha$, is calculated from a ratio of the
experimental molar conductivity and the ionic conductivity of fully dissociated ions

$$\alpha = \frac{\Lambda_{exp}}{\lambda_+ + \lambda_-}$$  \hspace{1cm} (1.38)

To determine the values for $\lambda_+$ and $\lambda_-$, measurements of the cation and anion
conductivities with non-complexing counter-ions are made along with those of a solution
of the non-complexing ions. For example, to determine the association constant for a
weak acid, HA, we must use a fully dissociating salt such as KCl. By measuring the
molar conductivity of HCl, KA and KCl, we can determine a molar conductivity value
for the fully dissociated acid, from the expression

$$\lambda_{H^+} + \lambda_A = (\lambda_{H^+} + \lambda_{Cl^-}) + (\lambda_{K^+} + \lambda_A) - (\lambda_{K^+} + \lambda_{Cl^-}) = \Lambda_{HCl} + \Lambda_{KA} - \Lambda_{KCl} = \Lambda_{HA}$$  \hspace{1cm} (1.39)
Once the association constant is determined, the limiting molar conductivity of an ion-paired solution can be determined using a modified version of the FHFP equation (Equation 1.20) which is shown below in Equation 1.40a. In addition, Equation 1.40a can be combined with the term for ion association given in Equation 1.35, which leads to the expression shown in Equation 1.40b:

\[
\Lambda = \alpha \left[ \Lambda^\circ - S \cdot (\alpha c)^{1/2} + E \cdot (\alpha c) \cdot \ln(\alpha c) + J_1 \cdot (\alpha c) - J_2 \cdot (\alpha c)^{3/2} \right] \quad (1.40a)
\]

\[
\Lambda = \Lambda^\circ - S \cdot (\alpha c)^{1/2} + E \cdot (\alpha c) \cdot \ln(\alpha c) + J_1 \cdot (\alpha c) - J_2 \cdot (\alpha c)^{3/2} - K_A \cdot \Lambda^\circ \cdot \gamma_s^2 \cdot \alpha \cdot c. \quad (1.40b)
\]

### 1.5.5 Association Constant Modelling

For studies of association or ionization constants, finding a model that will describe the change in the constant as a function of temperature and pressure is essential. The classical thermodynamic treatment for determining the association constant \( K_{T,p} \) at temperature \( T \) and pressure \( p \) is (Tremaine et al., 2004):

\[
\log K_{T,p} = \frac{\log K_{T_r,p_r} + \Delta H^\circ_{T_r,p_r} \left( 1/T_r - 1/T \right) + \int \frac{\Delta C_p^\circ}{T} dT}{R \ln 10} - \frac{1}{T} \int \Delta C_p^\circ dT - \int \frac{\Delta V^\circ}{T} dp, \quad (1.41)
\]

here \( T_r \) and \( p_r \) are the reference temperature and pressure respectively, \( R \) is the gas constant, \( H^\circ \) is the standard partial molar enthalpy, \( C_p^\circ \) is the standard partial molar heat capacity and \( V^\circ \) is the standard partial molar volume. This model is comprehensive, but requires expression for the temperature dependencies \( \Delta C_p^\circ \) and \( \Delta V^\circ \) to be known.

For solution chemistry, the temperature dependence of the association constant can be expressed using the density model developed by Marshall (1970):
\[ \log K = a + b / T + c / T^2 + [e + f / T + g / T^2] \log \rho, \quad (1.42) \]

here \(a, b, c\) are fitting parameters related to short range ionic interactions, \(d, e, f\) are fitting parameters related to long-range polarizations and \(\rho\) is the density of water. For the purposes of this study, the fitting parameters reported by Mesmer et al. (1988) for NaCl will be used to establish the outer limit of ion-pairing, as the degree of ion pairing decreases down the period for alkali halide salts (Quist and Marshall, 1969).

1.5.6 Ion Mobility/Walden Product

The conductivity of an ion in solution, \(\lambda^o\) is directly related to the viscosity of the solvent, \(\eta\), and ionic radius, \(r_{Stokes}\) through Stokes’ law (Robinson and Stokes, 1965)

\[ r_{Stokes} = \frac{z |F|^2}{(6\pi \eta N \rho \lambda^o)}, \quad (1.43) \]

for stick conditions where \(F\) is Faraday’s constant and \(N\) is Avagadro’s Number.

Walden’s rule predicts that the product of the limiting ion conductance and the solvent viscosity should be constant (Robinson and Stokes, 1965). That is:

\[ \frac{1}{r_{Stokes}} \propto \eta \lambda^o, \quad (1.44) \]

where the term \(\eta \lambda^o\) is referred to as the Walden product. Walden’s rule holds true for ions in organic solution, but fails for aqueous solutions (Kay, 1991), as ions have been shown to increase or decrease their Walden product with temperature. This discrepancy is explained by the Gurney-Frank-Wen model (Frank and Wen, 1957) which separates ions into three categories depending upon their effect upon the localized solvent structure that surrounds them.
Figure 1.8(i) shows a diagram depicting the three categories of ionic solvation. Their temperature dependence is shown in the Figure 1.8(ii), which is a plot of the change in Walden product with $T$ over the range 283 K to 318 K. Small ions with large charge density such as Li$^+$ and Et$_4$N$^+$ are depicted in Figure 1.8(i)(a). These do not exhibit any temperature effect on their Walden product. Large ions with low surface charge density such as I$^-$ and Cs$^+$ are depicted in Figure 1.8(i)(b). Such ions disturb the regional three dimensional hydrogen bonding in the solvent structure, decreasing the viscosity in the localized areas, and are known as ‘structure breakers.’ These ions have increased mobility at low temperatures where solvent structure is the greatest. Large ionic molecules with hydrophobic surfaces, such as Bu$_4$N$^+$ and Pr$_4$N$^+$ are depicted in Figure 1.8(i)(c). These cause an increase in the localized solvent structure due to the repulsion of surround solvent molecules, and are known as structure breakers and have decreased mobility at lower temperatures. These “structure-breaking” and “structure-making” effects are most influential at low temperatures. As the temperature is increased, the Walden product for all ions will eventually stabilize.

The use of the ratio of Walden products denotes changes in ionic mobility is not solely useful for temperature effects, but has also been applied to isotope effects as well (Swain and Evans, 1966; Broadwater and Evans, 1976). As the ionic mobility is dependent on the viscosity of the solvent, this relationship allows for a direct comparison of transport for ions in light and heavy water which will be discussed further in Section 3.4.
1.5.7 Proton Hopping Effects

The mobility of the hydrogen or deuterium-containing ions (H\(^+\), OH\(^-\), D\(^+\), OD\(^-\)) in water is higher than other ions with similar crystallographic radii. This is caused by two separate mechanisms of ionic movement: (i) the bulk ionic diffusion and (ii) proton hopping (also known as the ‘Grotthuss’ mechanism as reported by Conway et al. 1956). Proton hopping arises from a series of proton transfers as shown in Figure 1.9 (Tada et al., 1992). The H\(_3\)O\(^+\) ion causes the neighbouring water molecule to rotate, exposing a lone pair and creating a hydrogen bond. The local electric field drives the proton to transfer from the H\(_3\)O\(^+\) to the neighbouring water molecule. The newly formed H\(_3\)O\(^+\) ion causes the next neighbouring water molecule in the solvent to rotate, beginning the process anew. This rotation is caused by the repulsive effects between adjacent protons in the hydrogen bonded lattice.

Hydroxide undergoes a similar hopping mechanism, but it is less favoured due to lower repulsive forces between the OH\(^-\) molecule and the neighbouring water molecules (Tada et al., 1993). Deuterons and deuteroxide ions undergo the same time of hopping mechanism but, due to the greater mass of deuteron versus a proton the rotational step required to start the transfer is less energetically favourable.

To quantify the extra mobility arising from proton hopping, Tada et al. (1992, 1993) assumed that the bulk ionic diffusion of a H\(_3\)O\(^+\) ion was equivalent to that of a K\(^+\) ion, which has a similar crystallographic radii. Similarly, Cl\(^-\) was used to approximate the bulk diffusion of an OH\(^-\). The “excess” ionic conductivity that arises from proton hopping, \(\lambda^o_E\), was determined by the following relationships:

\[
\lambda^o_E(H_3O^+) = \lambda^o(H_3O^+) - \lambda^o(K^+)
\]  

(1.45)
The excess conductivity is dependent on neighbouring water molecules. Observing the change in the value of $\lambda^o_E$ with temperature will offer insight into the effect of changes in the hydrogen bonded structure of water to the mechanism of proton hopping from ambient to hydrothermal conditions. The light water work of Tada et al. (1992, 1993) reached a temperature of only 338 K, while the study presented here will reach values up to $T = 598$ K.

The work of Tada et al., (1992,1993,1994) also included a comparison between the proton hopping observed in light and heavy water at $T = 298$ K. They concluded that difference in excess conductivity is only dependent on the reduced mass, thus the ratio of the excess limiting conductivity of light water versus heavy water $[\lambda^o_E(H^+) / \lambda^o_E(D^+)]$ is approximately equal to $\sqrt{2}$. They further concluded that the difference for the excess conductivity of $OH^-$ versus $OD^-$ is dependent on both the reduced mass and the pre-rotation of the ions, thus the ratio of their excess limiting ionic conductivities $[\lambda^o_E(OH^-) / \lambda^o_E(OD^-)]$ is $\sim 2.2$.

1.5.8 Conductivity Modelling

Several models are reported in the literature that attempt to describe the limiting molar conductance of electrolyte solutions over wide temperature and pressure ranges based on their physical properties (Brummer and Hills, 1961; Smolyakov, 1968; Marshall, 1987; Oelkers and Helgeson, 1989; Zimmerman et al., 2012).

Brummer and Hills (1961) reported a simple correlation between the logarithm of the limiting conductivity and the inverse of the temperature. This takes the form:
\[ \log \Lambda^o = A + \frac{E_{a,p}}{RT}, \quad (1.47) \]

Here \( T \) is the temperature in Kelvin, \( R \) is the gas constant, \( E_{a,p} \) is the Arrhenius energy of activation of conductance at constant pressure and \( A \) is the pre-exponential fitting parameter.

The relationship reported by Smolyakov (1968) is of similar form to that of Brummer and Hill, but it represents the Walden product as a function of temperature. The Smolyakov equation is:

\[ \log \lambda^o \eta = A + \frac{E_\eta - E_\lambda^o}{RT}. \quad (1.48) \]

Here \( E_\eta \) is the activation energy of viscosity and \( E_\lambda^o \) is the activation energy of ionic conductance.

Marshall’s reduced state relationship, (Marshall, 1987) describes the limiting conductance of an aqueous electrolyte over a wide range of temperature (0-800 °C) and pressure (up to 400 MPa) by determining a reduced limiting equivalent conductance, \( \Lambda^o_{\text{r}} = (\Lambda^o/\Lambda^{oo}) \), and reduced equivalent solvent density, \( \rho_{\text{r}} = (\rho/\rho_h) \).

\[ \Lambda^o_{\text{r}} = 1 - \rho_{\text{r (elect)}} \quad (1.49) \]

Here \( \Lambda^{oo} \) is the value of \( \Lambda^o \) at a given temperature which is extrapolated to \( \rho = 0 \), and \( \rho_h \) (elect) is the extrapolated value of \( \rho \) which correspond to \( \Lambda^o = 0 \). Similarly, this model can be used to fit the reduced limiting conductance of a single ion (\( \lambda^o_{\text{r}} \)).

Oelkers and Helgeson reported a limiting equivalent conductance model, (Oelkers and Helgeson, 1989) that utilizes the Arrhenius activation energy in order to describe the electrolyte conductance over a wide temperature range (0-1000°C) and up to high pressures (500 MPa).
Here, $A_{Λ,e}$ is an Arrhenius pre-exponential factor and $E_{A,D,e,T}$ is the activation energy, both of which must be calculated using a number of designate temperature/pressure-independent regression coefficients. This model is quite rigorous, though it is more unwieldy than Marshall’s model as the calculation of the regression coefficients is a more labour-intensive process.

Recently, Longinotti and Corti (2009) reported a fractional Walden product based on concepts first reported by Bilz and Klemm (1926) and Pugsley and Westmore (1954):

$$\Lambda \eta^\alpha = \text{constant}. \quad (1.51)$$

The term $\alpha$ is a decoupling constant, which has a value close to 0.7 and differs based on the ions in solution. A similar equation was reported by Zimmerman et al. (2012) which represents limiting molar conductivities as a function of solvent viscosity and density:

$$\log \Lambda^\circ = \log A_1 + \left( A_2 + \frac{A_3}{\rho_w} \right) \cdot \log \eta. \quad (1.52)$$

The three empirical fitting parameters for each salt, $A_1$, $A_2$, and $A_3$ were found by least squares regression and $\rho_w$ is the solvent density in kg·m$^{-3}$. The $A_3/\rho_w$ term is required to fit high temperature data (Zimmerman et al., 2012).

1.6 High Temperature Solution Chemistry

1.6.1 Pioneering Work (Noyes)

Research in this field can be traced back to the Noyes et al. (1904, 1907, 1908) who conducted conductivity measurements on a variety of solutes at temperatures up to
306 °C and pressures up to 10 MPa. These measurements were conducting using a ‘conductivity bomb’, a static cell that was loaded with the solution to be measured and then placed in baths of known sequentially higher temperatures in which the solution resistance was measured. Noyes reported not only equivalent conductivities, but also ionization and ion-pair formation constants for a variety of salts. These measurements set the standard for conductivity measurements for nearly half a century and still compare favorably to modern work (Corti et al., 2004).

1.6.2 Static High Temperature Conductivity Cells

The 1950’s saw the development of high temperature and high pressure cells which could reach the conditions important for geochemical modelling. Franck et al. (1962) build a conductivity cell with a nickel-based alloy body and platinum-iridium inner tube to make measurements up to 800°C and 400 MPa. This design was later adapted and used at Oak Ridge National Laboratory by Marshall and his coworkers (Quist et al., 1965; Quist and Marshall, 1968, 1969) to measurement the temperature and pressure dependent association constants of ions from 0 to 800°C, including the only measurements of KI and CsI ever reported above 300°C. Additionally, the pressure system of the cell was temporarily modified to become a ‘flow-through’ type due to the corrosive nature of the ions under study (used for corrosive species).

More recently, this cell was used by researchers at Oak Ridge to very accurately measure conductivities of chloride and hydroxide solutions (Ho et al. 1994, 2000; Ho and Palmer, 1996, 1997, 1998) to within 0.1% precision at a range of temperatures from $T = 473$K to 873K and pressures up to 300MPa. This cell was permanently converted to a flow cell around the turn of the century. (Ho et al., 2001) to expand the possibilities for
experimental studies. The largest disadvantage to this cell is that it is only applicable for
a solute concentration range between 0.1 and 0.001 mol·L⁻¹ (Corti et al., 2004).

1.6.3 Flow High Temperature Conductivity Cells

The most important recent advancement in cell design has been the flow-through
cell developed at the University of Delaware by Wood and coworkers (Zimmerman et. al,
1995, Sharygin et al. 2002; Hnedkovsky et al.2005). This cell is able to accurately
measure solution conductivities at ionic strengths as low as 10⁻⁵ to 10⁻⁷ mol·kg⁻¹.
Additionally, the injection system and flow nature of the cell allows for more rapid
measurements, and eliminates systematic errors which leads to new experimental designs,
such as the one outlined in this thesis. Upon the retirement of Wood in 2008 this cell
came into possession of our group, where it was utilized for this study. The design and
operation of this cell will be presented in Chapter 2.

1.7 Thesis Objectives and Overview

This thesis reports the work that was completed during the course of my Master’s
studies at the University of Guelph. The experimental conductivity measurements were
done jointly, as a collaboration with Dr. Arcis, under Professor Tremaine’s supervision. The
calculations and modelling were my work, co-supervised by Dr. Arcis and Professor
Tremaine.

The objective of the project was to measure limiting molar conductivities of
binary salts in both light and heavy water to temperature up to or exceeding 573 K. A
method of determining transference numbers (outlined in section 1.4.4) was used to
determine the limiting ionic conductivities of each ion. Several fits were made to the experimental data to determine the best fitting strategy for the data across the temperature range. The resulting limiting ionic conductivities were used to calculate Walden product ratios, $R_{\text{Walden}}^{D/H}$, which allowed us to directly probe the differences in ionic transport between light and heavy water as well as comment on any changes in hydration over the temperature range. Finally, the contribution to conductivity that arises from proton hopping was determined using the method of Tada et al (1992).

Chapter 2 describes the experimental method utilized for this project, including solution preparation, conductivity cell design and repair and the conductivity flow system. The conductivity cell utilized was one of only two in North America that can be used to measure conductivities at the extremes of temperature and pressure reported in this thesis. Chapters 3 and 4 present the results and discussion for simple ions ($\text{Na}^+$, $\text{Cl}^-$, $\text{K}^+$, $\text{Cs}^+$, $\text{I}^{-}$) and proton hopping ions ($\text{H}^+$, $\text{D}^+$, $\text{OH}^-$, $\text{OD}^-$) respectively. This study contains the first reported values for conductivity for several ions in $\text{D}_2\text{O}$ at hydrothermal conditions. The excess conductivities arising from proton hopping are also reported for the first time above 338K for light water and heavy water. Finally, Chapter 5 presents the conclusions from this work and the next steps for continuing the project.
Table 1-1: Table of slope and intercept for plots of transference number $t^+_{\text{eq}}$ versus time using Equation 1.15 for NaCl and KCl in H$_2$O (Smith and Dismukes, 1963, 1964) Values are plotted in Figures 1.5 and 1.6.

<table>
<thead>
<tr>
<th></th>
<th>$m_t$</th>
<th>$b_t$ (H$_2$O)</th>
<th>$b_t$ (D$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>57.552</td>
<td>-0.010</td>
<td>-0.014</td>
</tr>
<tr>
<td>KCl</td>
<td>-25.679</td>
<td>0.103</td>
<td>0.094</td>
</tr>
</tbody>
</table>
Figure 1.1 Schematic of CANDU nuclear reactor (1) primary circuit (2) secondary circuit (3) boiler (4) condenser (5) fuel bundles (6) turbine
Figure 1.2 Schematic of Primary Circuit of Proposed SCWR Nuclear Reactor (1) primary circuit (2) condenser (3) fuel bundles (4) turbine
Figure 1.3 Equivalent circuit model, $C_{\text{cell}}$ capacitance of the cell, $C_D$ capacitance of the double layer, $R_s$ resistivity of solution, $R_{ct}$ resistivity of the charge transfer, $\alpha_w$ fraction of pure capacitance of the electrodes, $C_1$ capacitance at zero frequency
Figure 1.4 Nyquist plot of real portion of the impedance vs. the imaginary portion of the impedance (redrawn with modification from Hnedkovsky et al., 2005)
Figure 1.5 Plot of \( \log_{10}(t_{\text{Cl}}^\circ / t_{\text{Na}^+}^\circ) \) vs 1000/\( T/K \) for literature NaCl transference numbers (Longsworth, 1932; Allgood and Gordon, 1942; Smith and Dismukes, 1964)
Figure 1.6 Plot of $\log_{10}(t_{\text{Cl}^\circ}/t_{\text{K}^+})$ vs $1000/T$ for literature KCl transference numbers (MacInnes and Longsworth, 1932; Allgood et al., 1940, Smith and Dismukes, 1963)
Figure 1.7 Cartoon depicting (a): solvent-solvent separated ion pairing (SSIP) (b): solvent separated ion pairing (SIP) (c): contact ion pairing (CIP)
Figure 1.8(i) Three type of solvated ions: (a) ions whose Walden product is unchanged with Temperature (b) 'structure breaking' ions, whose Walden product decreases with temperature, (c) 'structure making ions' whose Walden product increases with Temperature; (ii) Plot of (Walden product at $T$ / Walden product at $10^\circ$C) versus $T$ for several simple ions. (reprinted from Kay, 1991 © IUPAC and DeGruyter)
Figure 1.9 Proton hopping mechanism reproduced from Erickson (2013) with permission
Chapter 2 Experimental Methods

2.1 D₂O Transfer and Purity

2.1.1 D₂O Transfer and Purity Analysis

Heavy water (D₂O) was supplied in a 50 kilogram carboy by Ontario Power Generation Ltd. This heavy water was distributed to one-litre bottles for ease of use. Deuterium atoms readily exchange with hydrogen atoms from moisture in the air (Deeny and O’Leary, 2009), requiring the D₂O transfer process to take place in an inert atmosphere with exacting protocols.

Fifty new 1 L polyethylene Nalgene bottles were washed using Versaclean detergent, and rinsed several times using various purities of water: four with tap water, four with deionized water and three with Nanopure (resistivity 18.2 MΩ·cm) water. The bottles were leached with Nanopure water for a period of 36 hours following the cleaning to remove any impurities in the bottles from the manufacturing process. After the leaching, the rinsing protocol was repeated. The bottles were then placed in an oven at 40°C for one hour to dry.

To ensure no contamination by atmospheric H₂O, the transfer was completed in a large glove box with a removable plexiglass wall. The size of the 50 kg carboy required us to load it into the box followed by as many of the Nalgene bottles as space would allow. The container was placed on two adjustable lab jacks to maintain the flow of the D₂O out of the dispenser cap. In addition, the container was tied to the roof of the glove box for added stability then the wall was replaced which sealed the contents. The glove
box was purged with N\textsubscript{2}(g). A representation of the inside of the glove box is given in Figure 2.1.

Prior to placing the carboy in the glove bag, a custom dispenser cap had been fitted onto the carboy using a small glove bag to replace the original cap as shown in Figure 2.2. The glove bag was taped to the carboy and filled with Ar(g), purging the bag four times before the regular cap was replaced with the dispenser cap. This dispenser cap was fitted with a stopcock to control the flow of the liquid, and a purging valve to allow the container to be purged by an inert gas.

The D\textsubscript{2}O transfer itself was completed in approximately 8 hours. Using the gloves attached to the plexiglass wall, each 1L bottle was slowly filled with D\textsubscript{2}O from the carboy then sealed tightly with its cap. Once filled, the bottles of D\textsubscript{2}O were transferred out of the glove box through the side chamber. This side chamber was purged independently of the main space, allowing for the full bottles to be removed and replaced with empty bottles while maintaining the inert atmosphere within the box. The seam between the cap and bottle was wrapped tightly with parafilm before each bottle was logged for storage.

D\textsubscript{2}O is classified as a nuclear substance meaning that its storage and use must be catalogued from time of its arrival until disposal. Each newly filled bottle of D\textsubscript{2}O was labelled with a primary stock code designation which was used to track the substance’s experimental use and later for proper disposal. In addition, the bottle creator (the person who completed the transfer) and mass of the D\textsubscript{2}O were recorded as part of the inventory process. These bottles were stored in the Physics Department radioactive storage vault.
2.1.2 Determination of Isotopic Purity of D₂O

The isotopic purity of the D₂O was determined by ¹H NMR using the method of Hamann and Linton (1977) at the time of transfer, and annually thereafter for the remaining stock. At the time of initial transfer, the purity was tested for the first and last bottle filled, while the annual test was conducted using a sample from a randomly selected unopened bottle remaining in storage.

Deuterated glacial acetic acid was used as an internal standard for determination of the isotopic purity. For the isotopic analysis of each bottle, four solutions of approximately 0.8 mol/kg CH₃COOD were prepared gravimetrically by weighing glacial deuterated acetic acid (99%, Sigma Aldrich, product #151777) into 30 mL Nalgene polyethylene containers which had been cleaned and leached using the process outlined in Section 2.1.1. These solutions were loaded into 5mm thin wall, 7”, 200 MHz NMR tubes (manufactured by Wilmad LabGlass – Part No. 506-PP-7). The NMR testing was completed by Dr. Andy Lo at the University of Guelph NMR Centre.

Two singlet peaks were observed for methyl and acetyl protons with a signal being three times greater for the methyl peak. Deuterium is a quadrupolar nuclei, possessing a spin = 1, meaning that it will not have a signal in ¹H NMR analysis. The protons and deuterons from the acetyl group will readily exchange with those of the solvent, whereas those attached to the methyl group do not (Hamann and Linton, 1977). By measuring the integrated peak area of the acetyl group as compared to the methyl group in the CH₃COOD in D₂O solutions, the concentration of ¹H in the solution can be determined.

To determine the isotopic purity, the number of water molecules that contained a proton, \( n_{HOD} \), was calculated.
\[ n_{\text{HOD}} = IP \cdot n_{\text{CH}_3\text{COOD}} \]  \hspace{1cm} (2.1)

where \( IP \) was the integrated peak ratio of the acetyl:methyl signals and \( n_{\text{CH}_3\text{COOD}} \) was the number of moles of \( \text{CH}_3\text{COOD} \) in solution, determined from the mass of \( \text{CH}_3\text{COOD} \) used in preparation of the solutions above. The number of moles of \( \text{D}_2\text{O} \), \( n_{\text{D}_2\text{O}} \), was given by the equation:

\[ n_{\text{D}_2\text{O}} = \frac{m_{\text{D}_2\text{O}} - (n_{\text{HOD}} \cdot M_{\text{HOD}})}{M_{\text{D}_2\text{O}}} \]  \hspace{1cm} (2.2)

where \( m_{\text{D}_2\text{O}} \) was the mass of \( \text{D}_2\text{O} \) obtained during solution preparation, and \( M_{\text{D}_2\text{O}} \) and \( M_{\text{HOD}} \) were the molar mass of \( \text{D}_2\text{O} \) and \( \text{HOD} \) respectively. Finally, the isotopic purity expressed as mol fraction percentages, \( \%_{\text{D}_2\text{O}} \), of the solution was calculated:

\[ \%_{\text{D}_2\text{O}} = (1 - \frac{n_{\text{HOD}}}{n_{\text{HOD}} + n_{\text{D}_2\text{O}}}) \cdot 100\% \]  \hspace{1cm} (2.3)

The purity range of the \( \text{D}_2\text{O} \) used for this study was between 99.698% and 99.665%, which was greater than the acceptable purity standard for \( \text{D}_2\text{O} \) for isotope effect studies, which is reported to be 99% (McDougall and Long, 1962, Arnett and McKelvey, 1969).

### 2.2 Solution Preparation

Aqueous 0.1 mol·kg\(^{-1}\) stock solutions of NaCl (Alfa Aesar Puratonic, 99.999%), KCl, (Alfa Aesar 99.95%), CsCl (Alfa Aesar 99.999%), KI (Alfa Aesar 99.9%) and CsI (Alfa Aesar 99.999%) in light and heavy water were prepared by mass from their anhydrous salts. Each salt was dried at 300°C until the mass difference between weighings was less than 0.02%. The stock solutions were prepared by mass with
Nanopure light water (resistivity 18.2 MΩ·cm) and heavy water provided by Ontario Power Generation (~99.7% purity).

Solutions of DCl (Aldrich 35 wt% solution), NaOH (Alfa Aesar 50% w/w), NaOD (Aldrich 40% wt% solution in D₂O, 99⁺ atom % D), KOH (Alfa Aesar 50% w/v) and KOD (Aldrich 40% wt% solution in D₂O, 99⁺ atom % D) were prepared by dilution to ~ 0.1 mol·kg⁻¹ with Nanopure light water or heavy water. HCl (Fluka, 0.1N standard solution), was used as is. The HCl and DCl solutions were standardized by quadruplicate titration against a known mass of THAM [tris(hydroxymethyl)aminomethane], while the NaOH, NaOD, KOH and KOD solutions were standardized by quadruplicate titration against known masses of KHP (potassium hydrogen phthalate).

Stock and diluted solutions samples for injection in the conductivity cell were prepared under argon to limit carbon dioxide contamination and to maintain isotopic purity of the D₂O solvent. High density polyethylene bottles were used for preparation and storage of salt and HCl/DCl stock solutions, while hydroxide solutions were prepared in high density polypropylene bottles. All stock bottles were washed to the specifications outlined in Section 2.1.

The target molality for the solutions measure by the conductivity cell was 1.0 x 10⁻³ mol kg⁻¹, thus the stock solutions required dilution prior to injection. For the non-hydroxide solutions, 250 ml Pyrex glass bottles with KIMAX GL-45 gas-tight tops were utilized for dilution and injection of the target solutions. The hydroxide solutions were prepared in 1 litre high density polypropylene Nalgene bottles with GL-38 gas-tight tops to avoid adsorption of the hydroxide species which would occur in glass containers. Each of the gas-tight lids consisted of a septum, an inlet gas tube and a connection port to the
conductivity cell. The stock solutions were diluted to the appropriate molality by the pure solvent by mass. The gas-tight bottles were filled under an argon atmosphere with a known mass of the target solvent followed by a syringe injection of a known mass of the stock solution (approximately 2 grams). The bottles were swirled manually to mix the solution and allowed to sit overnight before injection into the conductimeter.

2.3 High Temperature High Pressure Flow Conductimeter

2.3.1- Conductimeter Design and Assembly

The conductimeter utilized for this research is a novel high-temperature, high-pressure conductance flow cell that was built at the University of Delaware by Zimmerman et al. (1995), with improvements by Sharygin et al. (2002), Hnedkovsky et al. (2005) and Zimmerman et al. (2012). The great advantage to this flow cell is the short residence time of the solution, minimizing corrosion and adsorption effects on the electrodes. The temperature of the system is controlled to within 0.01K and is able to be maintained over the course of several days, ensuring that the experimental conditions stay constant for the entire sequence of solutions studied. Additionally the long period of data acquisition (85 to 100 minutes) provide several data points at a single temperature and pressure which were averaged to acquire very accurate solution impedances. (Zimmerman et al., 1995)

A schematic of the flow cell is shown in Figure 2.3. A temperature-controlled platinum tube (1.0 mm inner diameter, 1.6 mm outer diameter) carried the solution into a platinum-rhodium cup (1.6 mm inner diameter, 3.2 mm outer diameter) which served as the outer electrode. At the junction of the tube and cup, a diamond frit acts as a shield to
prevent back-flow of corrosion products. The inner electrode was a second platinum tube, with a small hole to carry the solution out the cell. A gold washer, annealed to the platinum-rhodium cup, to maintain the pressure seal, followed by a sapphire insulator and another annealed gold washer. The sapphire insulator provides electrical insulation between the two electrodes. Ceramic spacers surround the cell and inner electrode, to provide the electrical insulation and stability for the innermost parts of the cell. The body of the cell was constructed of solid titanium cylinders, held together with steel screws and Belleville washers. The entire cell assembly sits within a large air oven capable of controlling the temperatures to ± 0.15 K.

Temperature control of the cell was accomplished through use of three separate heating systems. The first heater was located inside the insulated box, which acts as a large air oven. The temperature was set to be approximately 5K lower than the target temperature of the cell and was controlled by an Omega CNi3254 proportional-integral-derivative (PID) controller. The temperature was measured by a Pt 1000 Ω resistance temperature detector (RTD). Two additional cartridge heaters, placed into holes drilled in the titanium block casing were utilized to heat the cell to the target temperature. This was controlled by a Leeds & Northrup 6430 Series Electromax III PID, while an additional Pt 1000 Ω RTD was used to measure the temperature of the cell. The solution entering the cell was preheated by a coil with a PID control feedback system. Two thermocouples, one attached at the fore of the inlet tube and another attached directly to the cell, coupled with an Automation Direct Solo 4824 PID system measured the heat difference between the solution and the cell and controlled the power of the heating coil to match the temperature of the solution to that of the cell. (Zimmerman et al., 2012)
2.3.2 Conductimenter Maintenance and Assembly

Due to the sustained extreme conditions within the cell, maintenance of the cell happens frequently, which requires that it be disassembled to provide access to interior components. There are a few different indicators that the cell requires maintenance. The most obvious indication of the cell requiring disassembly is when the sapphire insulator cracks, generating a loud noise but also affecting the cells’ electrical insulation which is apparent in the poor measurements of impedance between the electrodes. Large variations in pressure indicate that there is leak in the cell, which requires immediate attention as generally the pressure at a given temperature varies by less than 15kPa over the course of the entire array of injections. In addition, if the real-time Nyquist plot of the current measurement (monitored by Hewlett Packard VEE Version 6.1 software) does not have semi-circular shape as shown in Figure 1.4, this indicates that there are contaminants within the cell, which often requires its disassembly to rectify.

Upon the completion of this maintenance, proper re-assembly of the cell is of the utmost importance, as any leak may render the cell inoperable at higher temperatures and pressures. This task was completed by Mr. Casey Gielen, a machinist at the University of Guelph Machine Shop. When disassembled, the body of the cell consists of three pieces: the front of the cell, which houses the inlet tube; the main body of the cell; and the back end of the cell, consisting of the plunger piece.

Support rails, affixed to the front and middle pieces, were utilized in the assembly process. The front piece was clamped into place vertically, with the inlet tube pointed downward. The first gold washer was placed, lining up with the diamond frit, followed by the sapphire and the other gold washer. The outlet tube was placed through the
opening in the washers and sapphire, reaching down into the platinum cup. The ceramic disc and rocker were threaded down the outlet tube, followed by the ceramic cover, which was the final inner piece. The main body of the cell was placed next, ensuring that the support rails were in line with that of the front piece. Finally, the end piece was set into place by guiding the plunger down the centre of the main piece.

Long bolts were used for the front of the cell, and shorter bolts at the back end to connect the pieces of the cell together. All four bolts and their corresponding Inconel® Belleville washers were screwed into the cell at the same rate using a torque wrench, (i.e. each was given a single turn in sequence) ensuring that even pressure was distributed across the face of the cell. The bolts were hand tightened to start, but once a wrench was required, the bolts were tightened no more than one-sixth of turn before switching. After the cone shaped Belleville washer was flattened, extreme care was taken when tightening, as the ceramic in the cell may crack if too much pressure is applied. Once the pieces of the cell were secured together, the bolt at the front of the cell which houses the inlet tube was tightened, ensuring that the inner pieces of the cell were in tight contact. The cell was replaced in the oven and connected to the flow assembly, then pressure tested with water to ensure that no leaks were present. If leaks appeared the bolts at the front of the cell were further tightened before resuming experimental measurements.

2.3.3 Conductimeter Injection System

The injection system for the conductance apparatus is shown in Figure 2.4. The setup was similar to that described by Méndez de Leo and Wood (2005). The system consisted of a peristaltic pump, two high pressure liquid chromatography (HPLC) piston pumps, two six port injection valves and a Circle Seal Controls Inc. (Model
BPR21U25512 6000) psi back-pressure regulator which maintained the pressure at 20MPa.

The sample to be injected was loaded under Ar(g) into a stainless steel injection loop with a capacity of 50 mL by a peristaltic pump (Cole-Parmer Masterflex Easyload II 77201-60). Two Lab Alliance series 1500 HPLC pumps were used as part of the injection system. The first continuously injected Nanopure de-ionized water from a reservoir through the flow cell at a flow rate of 0.5 mL·min⁻¹. While the sample was being loaded into the injection loop, this water flow bypassed the sample loop and injected water directly into the cell. After the sample was fully loaded into the injection loop, the second HPLC pump pressurized the sample, then to complete the injection, the first pump was used to push the sample through the cell. The switching of lines before the injection was accomplished using two six port valve units. The injection process was computer-controlled using Hewlett Packard VEE Version 6.1 software, so that the switching of valves and operation of the pumps was fully automated.

2.3.4 Calculation of Cell Constant

Prior to making experimental measurements on the solutions of interest, the cell constant \( k_{cell} \) of the conductimeter was measured using a well-known calibration solution. This \( k_{cell} \) was equal to \( d/A \) as outlined in section 1.4.1. We have adapted the process used by Zimmerman and Wood (2002) in determining the constant of our cell.

The technique required impedance measurements of five KCl solutions ranging in molality from \( 10^{-4} \) to \( 10^{-2} \) mol·kg⁻¹ at \( T = 298.15K \) and \( P = \sim 20 \) MPa. A 4L glass bottle with an airtight KIMAX GL-45 cap, similar in design to that outlined in Section 2.1 was filled with argon and Nanopure light water (resistivity 18.2 MΩ·cm). The first injection
of the calibration process was strictly to measure the solution impedance of the Nanopure water. Prior to each subsequent injection, a known mass of a 0.32065 mol·kg⁻¹ stock solution of KCl was added to the bottle through the syringe port and mixed using a magnetic stirring bar and stir plate. The solution resistance measured by the conductimeter was compared to the equations provided Barthel et al. (1980), which allowed for the calculation of the $k_{cell}$ at 298 K and 0.1 MPa. Using thermal expansion coefficients for the inner components of the cell, the $k_{cell}$ at each temperature was calculated, using the method reported by Zimmerman et al., 2012.

### 2.4 Experimental Design

The solutions of interest were injected into the conductimeter in sequential order. Concerns regarding the dissolution of cell components by the KI and CsI solutions led to their removal from the injection schedule, to be replaced by CsCl. Additionally, NaOH and NaOD were added part way through the project to confirm some measurements from Kristy Erickson’s PhD project. Due to these changes, the entire array of solutions was not measured for every temperature. A typical sample injection plan is shown in Figure 2.5. The order of injection was: H₂O, D₂O, NaCl in H₂O, NaCl in D₂O, KCl in H₂O, KCl in D₂O, HCl in H₂O, DCl in D₂O, CsCl in H₂O, CsCl in D₂O, KI in H₂O, KI in D₂O, CsI in H₂O, CsI in D₂O, NaOH in H₂O, NaOD in D₂O, KOH in H₂O, KOD in D₂O, NaCl in H₂O, NaCl in D₂O, H₂O and D₂O. The final four injections were made to ensure that the conductivities measured at the beginning and end of each set of injections at a given temperature matched. This general sequence was repeated at $T = 298\text{K}, 373\text{K}, 423\text{K}, 473\text{K}, 522\text{K}, 548\text{K}, 573\text{K}$ and 598K at a pressure of $p = 20 \text{MPa}$. 
This injection design eliminated systematic errors that are inherent to static cell impedance measurements, which must be cooled and depressurized to change the sample between measurements, leading to difficulty in reaching the exact same experimental conditions for subsequent samples. The conductimeter used for this project could preserve the same temperature and pressure conditions over the course of many days, while the flow injection system allowed sequential measurements to be completed relatively quickly under the same conditions.

The flow rate of the cell was maintained at 0.5 mL·min\(^{-1}\). A minimum of 85 to 100 minutes was required to complete the data collection for each sample. Additionally, after each injection the injection loop and apparatus had to be flushed with deionized water from the reservoir for a period of 30 to 100 minutes to eliminate any traces of the previous sample solution. The rinsing period was visually monitored using the VEE software, when the impedance of the solution returned to the value for H\(_2\)O, the next injection could be administered. Each individual solution required a minimum of 2.5 hours to complete a measurement. The entire set of solutions required a minimum of 55–60 hours for each temperature.

### 2.5 Experimental Precision

To estimate the uncertainty of the measurements for the AC conductivity instrument, that we have utilized several different methods. As mentioned in Section 2.4, we measured NaCl at the beginning and end of each set of measurements to ensure that the equipment was returning accurate values over the entire run. Table 2.1 shows the values for limiting molar conductivity in light and heavy water for NaCl from \(T = 373\) K.
to 598 K. The difference between the measured values for same solution at the beginning and the end of the 5 – 8 day injection series being less than ±1 % across the entire temperature range. We therefore consider the precision of our values for Λ and the accuracy of these values relative to one another to be ≤ 1%.

The recently submitted Ph. D. thesis of Kristy Erickson (2013) includes a comparison of literature values of molar conductivity to the for KCl, NaCl and HCl measured for her project. The comparison showed that the experimentally measured values agree with the literature to within ±5%, which is adopted as the absolute accuracy of the measurements presented in Chapters 3 and 4.

The conductivity model expressed in equation 1.52 was determined to be the best fit to the experimental data, for reasons that will be outlined in Section 3.3.2. By fitting the model across the entire temperature range, then comparing the calculated values to the experimental values, the linearity of the data can be determined. The fit of Equation 1.52 for NaCl and KCl in H₂O when compared to the experimental data yields an average relative error of ±2.0 % and 2.2 % respectively. Despite the bias from the fitting equation caused by it not being a perfect model, the low error indicates that the data across the temperature range is accurate with very few outliers.
Table 2-1 Table of limiting molar conductivities of NaCl in H₂O and D₂O measured at the beginning (#1) and end (#2) of a set of injections at a given temperature

<table>
<thead>
<tr>
<th>T / K</th>
<th>( \Lambda^\circ(\text{NaCl}) \text{ H}_2\text{O} \ #1 )</th>
<th>( \Lambda^\circ(\text{NaCl}) \text{ H}_2\text{O} \ #2 )</th>
<th>( \Lambda^\circ(\text{NaCl}) \text{ D}_2\text{O} \ #1 )</th>
<th>( \Lambda^\circ(\text{NaCl}) \text{ D}_2\text{O} \ #2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>373.150</td>
<td>352.43</td>
<td>355.94</td>
<td>309.80</td>
<td>309.86</td>
</tr>
<tr>
<td>423.308</td>
<td>518.13</td>
<td>523.90</td>
<td>458.20</td>
<td>459.90</td>
</tr>
<tr>
<td>473.074</td>
<td>683.66</td>
<td>687.66</td>
<td>613.48</td>
<td>617.48</td>
</tr>
<tr>
<td>522.876</td>
<td>826.12</td>
<td>831.02</td>
<td>747.70</td>
<td>750.32</td>
</tr>
<tr>
<td>548.100</td>
<td>864.44</td>
<td>863.97</td>
<td>812.48</td>
<td>811.41</td>
</tr>
<tr>
<td>572.800</td>
<td>929.81</td>
<td>929.32</td>
<td>877.93</td>
<td>878.20</td>
</tr>
<tr>
<td>597.931</td>
<td>996.77</td>
<td>999.57</td>
<td>950.83</td>
<td>954.48</td>
</tr>
</tbody>
</table>
Figure 2.1: Glove Box Interior Setup for Heavy Water Transfer (Courtesy of Hugues Arcis)
Figure 2.2 Schematic summarizing the exchange of the carboy cap with the dispenser cap (Courtesy of Hugues Arcis)
Figure 2.3: Schematic of the AC flow conductance cell: (1) platinum inlet tube; (2) platinum outlet tube; (3) diamond frit; (4) ceramic spacer; (5) Inconel® Belleville washers; (6) sapphire insulator; (7) titanium ram; (8) steel screws; (9) platinum outer electrode; (10) platinum inner electrode. (adapted from Zimmerman et al., 1995)
Figure 2.4: Schematic of the high pressure sample injection system: (1) Pyrex or Nalgene solution bottles; (2) peristaltic pump; (3) delay loop; (4) six-port injection valves; (5) HPLC pumps; (6) deionized water reservoir; (7) back pressure regulator; (8) temperature-controlled insulated air oven; (9) conductance cell; (10) pressure transducer; (11) waste solution reservoirs; (12) Argon tank (adapted from Zimmerman et al., 2012)
Figure 2.5 Injection order for set of solutions in the conductimeter
Chapter 3 Limiting Conductivities of Salts in H\textsubscript{2}O and D\textsubscript{2}O

3.1 Introduction

This chapter will present the measurement of limiting molar conductivities, \( \Lambda^\circ \), of simple binary salt solutions in light and heavy water, made in the temperature range \( T = 298 \) to \( 598 \) K at \( p = 20 \) MPa using the conductimeter flow system and experimental design described in Chapter 2.

Limiting ionic conductivities, \( \lambda^\circ \), have been calculated by using an extrapolation of the transference number work of Smith and Dismukes (1963, 1964) to these experimental conditions and an assumption regarding the transference change with temperature in heavy water compared to light water. Several theoretical models for ionic conductivity have been fitted to the experimental data so that we could choose the most suitable model for the temperature range of the experiment.

Ratios of Walden products have been calculated to examine differences in ionic conduction for each ion in light and heavy water (Swain and Evans, 1964). These ratios allow us to compare differences in transport and ionic solvation for ions in H\textsubscript{2}O and D\textsubscript{2}O.

3.2 Limiting Molar Conductivities \( \Lambda^\circ \)

Experimental results for NaCl, KCl, CsCl, CsI and KI in both H\textsubscript{2}O and D\textsubscript{2}O are tabulated in Tables 3.1 and 3.2. The solutions are listed according to temperature and include the density of the solvent. The concentration is tabulated both as molarities, \( c = \ldots \)
mol of solute·(L of solution)$^{-1}$ and in molalities, $m = \text{mol of solute·(kg of solution)$^{-1}$. To determine the solution concentration, it was assumed that the apparent molar volume was equal to the standard partial molar value, $V_c = V^\circ$, which allowed for us to make an accurate estimation of the solution density, $\rho_{\text{soln}}$, from the expression (Klotz and Rosenberg, 1972)

$$\rho_{\text{soln}} = \frac{(M_s \cdot \rho_{H_2O} \cdot m) + (1000 \cdot \rho_{H_2O})}{(V^\circ \cdot \rho_{H_2O} \cdot m)} \quad (3.1)$$

where $M_s$ is the molar mass of the solute. This approach is more accurate than the assumption that $\rho_{\text{soln}} = \rho_w$ that is commonly used. Standard partial molar volumes were calculated using the program SUPCRT (Johnson et al., 1992) which uses the Helgeson-Kirkland-Flowers equation to determine standard partial molar thermodynamic properties. The concentration was calculated using the mass of the solvent $w_1$ and the mass of solute $w_2$:

$$c = \frac{\rho_{\text{soln}} \cdot m \cdot w_1}{w_1 + w_2} \quad (3.2)$$

The specific conductivities, $\kappa$ and the corresponding molar conductivities, $\Lambda^{\text{exp}}$ are also tabulated in Tables 3.1 and 3.2. The limiting molar conductivities, $\Lambda^\circ$ were calculated using the FHFP equation described in Section 1.5.2.

The limiting molar conductivity of each species is plotted as a function of temperature in Figure 3.1 ($H_2O$) and Figure 3.2 ($D_2O$). The plots show an increase in conductivity with temperature for all solutions, consistent with the qualitative behaviour predicted by Stokes Law. The trend indicates that the conductivity for all ions with the exception of $Na^+$ is quite similar across the temperature range from $T = 298.162$ K to $T = 597.931$ K.
The solid line in these plots is from the fit of Equation 1.52 to the data. This equation proved to be the most suitable fit of those outlined in Section 1.5.8. The fitting methodology will be discussed further in the next section.

3.3 Single Ion Conductivity $\lambda^o$

3.3.1 Transference Number Extrapolations

As literature values for the transference numbers of ions in D$_2$O only exist at ambient conditions, we had to assume that the change in transference number with temperature is the same in light and heavy water. Thus, the parameters for Equation 1.15 listed in Table 1-1 for K$^+$ and Na$^+$ in H$_2$O, could be used to determine the change in $t^o$ in D$_2$O at hydrothermal conditions by using the same values for the $m_t$ parameter to reproduce the slope of the line and scaling the $b_t$ parameter to reproduce literature values in D$_2$O (Swain and Evans, 1966; Nakahara, 1985). The results are listed in Table 1-1 and shown in Figure 3.3 for NaCl and Figure 3.4 for KCl.

In order to calculate the limiting ionic conductivity values for our entire temperature range, we had to extrapolate the existing literature values to hydrothermal conditions, as the highest reported transference numbers for NaCl and KCl in light water were at 398 K and 388 K respectively (Smith and Dismukes, 1963 and 1964.) Equation 1.15, with the parameters from Table 1-1 was used to extrapolate the transference numbers to higher temperatures in both H$_2$O and D$_2$O as shown in Figure 3.5 for NaCl and Figure 3.6 for KCl. The extrapolated values for $t^o_{\text{Cl}^-}$ in H$_2$O are tabulated in Table 3-3 and in Table 3-4 for D$_2$O. These values were used to calculate $\lambda^o$ for Cl$^-$. 
A plot of the limiting conductivity of chloride ions $\lambda^\circ(\text{Cl}^-)$ from Tables 3.3 and 3.4, split using both the NaCl and KCl transference number extrapolations, is shown in Figure 3.7 along with single ion literature values from Zimmerman et al. (2012). This plot shows that the values of $\lambda^\circ(\text{Cl}^-)$ obtained from either set of transference numbers are quite close, with a maximum relative error of $\leq 2.5\%$. Comparison of values from Zimmerman et al. (2012) with the experimental values results in a maximum difference between these critically evaluated “best” values for Cl$^-$ from NaCl and KCl varying by $\leq 5\%$ and $\leq 2.5\%$ respectively over the temperature range, with the greatest variance at high temperature. Literature values of NaCl and KCl from Ho et al. (1994, 2000), were split using our transference number values up to 673 K, with a maximum standard error of 2%. The large discrepancy at $T = 673$K is because to the studies of Ho et al. (1994, 2000) took place at different pressures (NaCl, $p = 32.53$ MPa; KCl, $p = 29.75$ MPa) The solution viscosities were used to correct the values to our experimental conditions using Walden’s rule. Either the correction was inaccurate or the combined experimental uncertainties are large at $T = 673$K. Transference numbers for KCl were chosen as the values of $\lambda^\circ(\text{Cl}^-)$ from KCl were in between experimental and literature values of NaCl.

### 3.3.2 Limiting Ionic Conductivities

The limiting ionic conductivities, $\lambda^\circ$ of Cl$^-$, K$^+$, Na$^+$, Cs$^+$ and I$^-$ in light and heavy water were calculated from the $\Lambda^\circ$ data in Tables 3-1 and 3-2. These values were split using the extrapolated transference numbers discussed above. The $\lambda^\circ$ values for the ions studied in this project are tabulated in Table 3-3 and Table 3.4 and plotted as a function of temperature in Figure 3.8 ($\text{H}_2\text{O}$) and Figure 3.9 ($\text{D}_2\text{O}$). Once the calculated $\lambda^\circ$ values
for Cl\(^-\) was determined, the other limiting ionic values were determined by stepwise subtraction. For instance, to determine the \(\lambda^o\) for Cs\(^+\), the \(\lambda^o\) value for Cl\(^-\) was subtracted from the \(\Lambda^o\) for CsCl and the uncertainty \(\delta \lambda^o\) is calculated from:

\[
\lambda^o (\text{Cs}^+) = \Lambda^o (\text{CsCl}) - \lambda^o (\text{Cl}^-) \quad (3.3a)
\]

\[
\delta \lambda^o (\text{Cs}^+) = [\delta \Lambda^o (\text{CsCl})^2 - \delta \lambda^o (\text{Cl}^-)^2]^{1/2} \quad (3.3b)
\]

For the purpose of this study, the transference numbers for KCl were used in preference to those for NaCl for two reasons: (i) determining very accurate values for K\(^+\) and Cl\(^-\) in solution is imperative for this project, as will be outlined in Chapter 4, and (ii) a greater number of our solutions included K\(^+\) ions versus Na\(^+\) ions (KCl, KOH, and KI vs. NaCl and NaOH). The values of ionic conductivity are determined by stepwise subtraction. The value for \(\delta \lambda^o (\text{Cl}^-)\) was taken to be the same as for \(\delta \Lambda^o (\text{KCl})\) in Table 3.1. The determination of \(\delta \lambda^o (\text{Cs}^+)\) is shown in Equation 3.3b. Effectively, for every ion removed from initial split ions (in this case, K\(^+\) and Cl\(^-\)) the propagation of error limits increases. This means that by using the KCl scheme, we minimize the compounded error that it attributed to each ionic conductivity value.

The ordering of the ions in Figures 3.8 and 3.9, with Na\(^+\) being the least conductive, followed by K\(^+\), Cs\(^+\), Cl\(^-\) and I\(^-\) showing the greatest mobility.

As mentioned in Section 3.2, the solid line is the fit of Equation 1.52 (Zimmerman et al., 2012) to the experimental data. To determine the best fitting equation to use for the temperature range of the study, each equation from Section 1.5.8 was fitted to the experimental data to determine that which best represented the experimental results with the fewest terms and smallest standard error. Equations 1.49 and 1.50 were not considered, as we sought an equation that was a function of the solvent viscosity and/or
density. Additionally, several empirical methods were tested, with the best fit arising from the equation:

\[ \log \lambda^o = \frac{A_1 + \frac{A_2}{T}}{\log \eta} \]  

(3.4)

where \( A_1 \) and \( A_2 \) are fitting parameters.

The calculated fitting parameters for Equations 1.47, 1.48, 1.52 and 3.4 are presented in Table 3-5. The relative error of each fitting equation for each ion is plotted in Figure 3.10 (H\(_2\)O) and Figure 3.11 (D\(_2\)O). Relative error is defined as:

\[ \text{Relative Error} = \frac{\lambda_{fit}^o - \lambda_{exp}^o}{\lambda_{exp}^o} \]  

(3.5)

The standard relative error and standard deviation for the remaining equations are listed in Table 3-6. The standard relative error is calculated by the following:

\[ \text{Standard Relative Error} = \left[ \frac{1}{n} \sum_{i=1}^{n} \left( \frac{\lambda_{fit}^o - \lambda_{exp}^o}{\lambda_{exp}^o} \right)^2 \right] / n \]  

(3.6)

where \( n \) is the number of temperatures where each ion was measured. The standard deviation is the square root of the relative standard error.

The fits for Equation 1.47 (Brummer and Hills, 1961) and the empirical fit, Equation 3.4 had the highest average deviation from the experimental values. Equation 1.48 (Smolyakov, 1968) and Equation 1.52 (Zimmerman et al, 2012), deviated significantly less than those mentioned above. Additionally the period of the relative error plots was smaller, indicating that these models don’t grossly overestimate the conductivity in the range \( T = 375 \) K to \( T = 525 \) K in the same way as the other models. Equation 1.52 reported by Zimmerman et al. (2012) proved to be the best for representing
the limiting ionic conductivity as it yielded the lowest standard deviation while also providing the relative error plot with the shortest interval above and below zero.

Additional considerations regarding the fitting equation will be discussed in Section 4.4.

In the case of the alkali metal ions and halide ions, the $A_3$ term in equation 1.52 (Zimmerman et al, 2012) was not found to be significant, thus the model for these ions is density independent, and the calculation of the conductivity requires only the solvent viscosity.

A plot of the ratio of the Walden product at a given temperature divided by the Walden product at $T = 298K$

$$R_{T/298K}^{Walden} = \frac{(\eta^w T)}{(\eta^w 298K)} = \frac{r_{stokes-298K}}{r_{stokes-T}}$$

is shown in Figure 3.12 for the ions studied here. This plot is similar to the plot in Figure 1.8(ii), but the temperature range has been greatly increased. Values that deviate greatly from parity indicate a larger structure breaking effect at ambient conditions. The plot shows that $Na^+$ is the least structure breaking ion in solution, followed by $\Gamma$ and $Cl^-$, with $K^+$ and $Cs^+$ showing the greatest decrease in Walden product over the temperature range.

### 3.4 Walden Product Ratios

The Walden product ratio is useful for comparing the efficiency of ionic transport mechanism in solution in light and heavy water. A direct comparison of the Walden product for ions in D$_2$O and H$_2$O yields the relationship:

$$R_{D/H}^{Walden} = \frac{(\eta^w D_2O)}{(\eta^w H_2O)} = \frac{r_{stokes-H_2O}}{r_{stokes-D_2O}}$$
henceforth known as the Walden product ratio. If the efficiency of ionic transport
mechanism of an ion in solution is the same in both solvents, \( R^{D/H}_{\text{Walden}} \) will be equal to 1. If
\( R^{D/H}_{\text{Walden}} > 1 \) the ions diffuse more readily in heavy water, while a \( R^{D/H}_{\text{Walden}} < 1 \) indicates
more efficient transport mechanism in light water. Tracing the \( R^{D/H}_{\text{Walden}} \) change with
temperature will offer insight into the changes in mobility for the ions in light and heavy
water solutions, most notably as it relates to ionic solvation.

The Walden product ratios for the ions were calculated from the physical
properties in Table 3-7 and Table 3-8 and are tabulated in Table 3-9. Plots of the Walden
product ratio over the experimental temperature range are shown in Figure 3.13 and
Figure 3.13. The solid line is the fit of the equation by Zimmerman et al. (2012)
(Equation 1.52) to the experimental data. The fitted values of \( \lambda^o \) for the ions lie within the
experimental uncertainty error of \( R^{D/H}_{\text{Walden}} = 1.0 \pm 0.10. \)

3.5 Discussion

The accuracy of the values \( \lambda^o(\text{Cl}^-) \) obtained from the transference number
extrapolations in Section 3.3.1 was assessed by comparing experimental and literature
values below \( T = 673 \) K. First, the values of \( \lambda^o(\text{Cl}^-) \) from our experimental NaCl data as
shown in Figure 3.7 agreed to within 5% with those reported from the fit of literature
values of \( \lambda^o(\text{Cl}^-) \) from NaCl by Zimmerman et al. (2012). Second, the values for \( \lambda^o(\text{Cl}^-) \)
from the experimental KCl data chosen for this thesis were 2.5% below the values from
Zimmerman et al.’s (2012) fit, and 2.5% above values from our experimental NaCl data.
From this, we assign uncertainty limits of ± 3% in accuracy to the values of λ°(Cl⁻) in Tables 3.3 and 3.4.

The limiting conductivities in Table 3.3 at ambient conditions are traditionally described by the Gurney-Frank-Wen model for ionic hydration (Frank and Wen, 1957). At T = 298 K, the ionic conductivity of the Na⁺ ion is significantly less than the other ions in solution (K⁺, Cs⁺, Cl⁻, I⁻). The ions listed parenthetically are all considered to be “structure-breaking” ions based on their conductivity behaviour at ambient conditions as described in Section 1.5.6. This effect is thought to arise because they have low surface charge density which disturbs the local hydrogen bonded network in water around them, effectively decreasing the local viscosity. Sodium ions have a small ionic radius, with a tightly held first hydration shell and as such do not have any great effect on the local solvent structure beyond the first shell. The limiting conductivity of the sodium ion is only 69% of the average conductivity of the other ions (K⁺, Cs⁺, Cl⁻, I⁻) in H₂O and 63% for D₂O.

The Gurney-Frank-Wen model is based on data up to 318 K, much below our experimental temperature range, but we will discuss our results using the same theory. Over the experimental temperature range, the Stokes’ radii increase in the order Na⁺ < I⁻ < Cl⁻ < K⁺ < Cs⁺ (see Figure 1.8(ii) and Figure 3.12). Sodium would be expected to have the lowest conductivity, as its structure breaking properties are significantly weaker than the other ions. According to the review by Seward and Driesner in 2004, the sodium ion has a more tightly bound primary solvation shell, meaning that the Stokes radius experiences a smaller comparative change across the temperature range. The interactions between the solvation shell and the changing bulk solvent structure are less impactful
over the experimental temperature range. For the larger ions, the primary solvation shell is less tightly held, resulting in a more rapid increase in Stokes radius. These ions experience an expansion of their hydration shell even with an accompanied loss of coordinated solvent molecules.

At $T = 598$ K, the conductivity of the sodium ion has reached 84% of the average conductivity of the other ions in H$_2$O, and 89% in D$_2$O, an increase of 15% and 26% respectively. This confirms that the limiting conductivities of a structure breaking ion are lower at elevated temperatures compared to the less structure breaking ion. In addition, the changeover in comparative Walden product ratios for sodium in H$_2$O versus D$_2$O at high temperature confirms that the structure breaking ions have a greater localized effect on the solvent viscosity in D$_2$O. This also suggests that as the temperature is increased, the “structure” of D$_2$O decreases at an accelerated rate compared to that of H$_2$O, as has been shown in the literature (Kell, 1972).

Of the four structure-breaking ions, two trends are evident for the experimental data. The first is that the alkali metal ions have a lower conductivity than the halides of similar crystallographic radii, i.e. $\lambda^o(\text{I}^-) > \lambda^o(\text{Cs}^+) \text{ and } \lambda^o(\text{Cl}^-) > \lambda^o(\text{K}^+)$. This is to be expected, as the charge to radius ratio is greater for the halides than for the alkali metals species. When an identical voltage is applied, the species with the greater charge to radius ratio would be expected to be more mobile. This is in agreement with Stokes Law, where the effective radius of the ion is inversely proportional to its efficiency of ionic transport mechanism. In addition, the plot of the ratio of the Walden products at temperature $T$ to the Walden product at ambient conditions shown in Figure 3.12 indicates that the Cs$^+$ and K$^+$ ions have a greater structure breaking effect than I$^- \text{ and Cl}^-$. This explains why the
conductivities of these ions are the same at $T = 298$ K, but increase at a greater rate for the anions than the cations.

The second observed trend is the more interesting: within the classes of ions (alkali metal and halide), the ion with the smaller ionic radius has the lower conductivity, which is contrary to Stokes Law. This trend can be attributed to the changes in hydration with temperature. In the case of the chloride ion, the coordinated number of water molecules has been shown to increase (Yamanaka et al., 1993; Driesner et al., Yamaguchi and Soper, 1999) with temperature, though there is some disagreement about the magnitude of the increase (Seward and Driesner, 2004) The coordination for iodide ions with temperature has been shown to decrease with temperature (Seward and Driesner, 2004). As the efficiency of transport of an ion is proportional to the radius of the solvation shell, the decrease in the solvation for iodide coupled with the increase for chloride over the temperature range would support the trend observed experimentally.

For the alkali metal species, there is only a single study conducted at ambient conditions for potassium (Palinkas et al., 1980), while for cesium, there is a study from 298K to 373 which shows no change in coordination number. (Seward and Driesner, 2004). Should these ions exhibit the same change in coordination as their corresponding halides, their comparative conductivities can be attributed to the change in solvated ionic radius, however we are lacking the experimental results to state this conclusively.

The Walden product ratio plots shown in Figure 3.13 and Figure 3.13 indicate that the difference in ionic radii between ions in light and heavy water is minimal. There are some small variations, particularly at ambient temperatures which can be explained by the nature of the solvent and the ions. For potassium, chloride and cesium ions, $R_{Walden}^{D/H}$ is
greater than 1 for low temperatures, indicating greater transport in D₂O. As discussed above, the structure breaking qualities of these ions seem to lower the local viscosity in D₂O by a greater magnitude than in H₂O. As temperature increases, the solvent becomes less structured which decreases the structure breaking effect, levelling the ionic mobility for the two solvents. For sodium at $T = 298K$, the value for $R_{Walden}^{D/H}$ is less than 1, indicating transport is more favoured in light water. This is due to the sodium ion being hindered by the more structured D₂O solvent. As the temperature increases, the solvent structure quickly breaks down (Kell, 1972) allowing the ion to move more freely through the solution. For the iodide ion, the results contravene what would be expected. Iodide is also a structure breaking ion, and should have a $R_{Walden}^{D/H}$ greater than 1 as observed for K⁺, Cs⁺, and Cl⁻, but the opposite is the case. There is no theoretical support to explain the mobility of the iodide ion being greater in H₂O than in D₂O at ambient conditions, and this discrepancy must be attributed to the experimental uncertainty, which is equal to ± 13 % for the $R_{Walden}^{D/H}$ of I⁻.

The general trends in the plots of $R_{Walden}^{D/H}$ indicate that the mobility of the ions in light and heavy water is the same, particularly at high temperatures. The transport of these ions is most highly dependent on the viscosity of the solvent, not on the solvent itself. Though some of the ions are exhibiting trends upwards or downwards, this solvent effect is likely due to the fact that D₂O is more structured than H₂O at ambient conditions (Jancso and Van Hook, 1974), thus the structure breaking ions have a greater effect on the surrounding solvent hydrogen bonds.
Table 3-1: Values of Experimental Molar Conductivities, $\Lambda_{\exp}$, and Fitted Limiting Molar Conductivities, $\Lambda^\ast$, for NaCl$_{\text{aq}}$, KCl$_{\text{aq}}$, CsCl$_{\text{aq}}$, KI$_{\text{aq}}$, and CsI$_{\text{aq}}$ in H$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

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<th>solute</th>
<th>$m_{\text{aq}} \times 10^6$ (mol•kg$^{-1}$)</th>
<th>$c \times 10^6$ (mol•L$^{-1}$)</th>
<th>$\kappa \times 10^6$ (S•cm$^{-1}$)</th>
<th>$\Lambda_{\exp}$ (S•cm$^2$•mol$^{-1}$)</th>
<th>$\Lambda^\ast$ (S•cm$^2$•mol$^{-1}$)</th>
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</thead>
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<tr>
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<td>163.47 ± 1.63</td>
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<tr>
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<td>KI (aq)</td>
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<td>976.66 ± 9.77</td>
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<td>CsI (aq)</td>
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Table 3-2: Values of Experimental Molar Conductivities, $\Lambda_{\text{exp}}$, and Fitted Limiting Molar Conductivities, $\Lambda^\circ$, for NaCl\,(aq), KCl\,(aq), CsCl\,(aq), KI\,(aq), and CsI\,(aq) in D$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

<table>
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<tr>
<th>Solvent</th>
<th>$m_{\text{aq}} \cdot 10^6$ (mol $\cdot$ kg$^{-1}$)</th>
<th>$c \cdot 10^6$ (mol $\cdot$ L$^{-1}$)</th>
<th>$\kappa \cdot 10^6$ (S$\cdot$cm$^{-1}$)</th>
<th>$\Lambda_{\text{exp}}$ (S$\cdot$cm$^2$$\cdot$mol$^{-1}$)</th>
<th>$\Lambda^\circ$ (S$\cdot$cm$^2$$\cdot$mol$^{-1}$)</th>
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</thead>
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<td>100.12</td>
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<td>350.00 $\pm$ 3.50</td>
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<td>514.61 $\pm$ 5.15</td>
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Table 3-3 Values of Fitted Limiting Ionic Conductivities, $\lambda^{\circ}$, for Cl$^{\text{aq}}$, K$^{+}\text{(aq)}$, Na$^{+}\text{(aq)}$, Cs$^{+}\text{(aq)}$ and I$^{\text{aq}}$ in H$\text{O}$ from $T = 298 \text{ K}$ to $T = 598 \text{ K}$ at $p = 20 \text{ MPa}$

<table>
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<tr>
<th>$T$ ($K$)</th>
<th>$t^{\circ}$ Cl$^{-}$</th>
<th>$\lambda^{\circ}(\text{Cl})$</th>
<th>$\lambda^{\circ}(\text{Na}^+)$</th>
<th>$\lambda^{\circ}(\text{K}^+)$</th>
<th>$\lambda^{\circ}(\text{Cs}^+)$</th>
<th>$\lambda^{\circ}(\text{I}^-)$</th>
<th>$\lambda^{\circ}(\text{Cs}^+)$</th>
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$\delta\lambda^{\circ}/\lambda^{\circ}$

| a: from $\Lambda^{\circ}$ (CsCl) | ±0.010 | ±0.014 | ±0.010 | ±0.014 | ±0.014 | ±0.017 |
| b: from $\Lambda^{\circ}$ (CsI)  |        |        |        |        |        |        |
| c: precision relative to other ions measure in thesis |        |        |        |        |        |        |

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Table 3-4 Values of Limiting Ionic Conductivities, $\lambda^\circ$, for Cl$_{aq}$, K$^+$$_{aq}$, Na$^+$$_{aq}$, Cs$^+$$_{aq}$ and I$_{aq}$ in D$_2$O from $T =$ 298 K to $T =$ 598 K at $p =$ 20 MPa

<table>
<thead>
<tr>
<th>$T$ (K)</th>
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<th>$\lambda^\circ$ (Na$^+$)</th>
<th>$\lambda^\circ$ (K$^+$)</th>
<th>$\lambda^\circ$ (Cs$^+$)$_a$</th>
<th>$\lambda^\circ$ (I$^-$)</th>
<th>$\lambda^\circ$ (Cs$^+$)$_b$</th>
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$\delta \lambda^\circ / \lambda^\circ$ $^c = \pm 0.010 \pm 0.014 \pm 0.010 \pm 0.014 \pm 0.014 \pm 0.017$

a: from $\Lambda^\circ$ (CsCl)
b: from $\Lambda^\circ$ (CsI)
c: precision relative to other ions measure in thesis
Table 3-5 Fitting parameters for limiting ionic conductivity fitting equations (Brummer and Hills, 1961; Smolyakov, 1968; Zimmerman et al. 2012)

<table>
<thead>
<tr>
<th></th>
<th>Equation 1.147</th>
<th>Equation 1.48</th>
<th>Equation 1.52</th>
<th>Equation 3.4</th>
</tr>
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<td>$E_{a,p}$</td>
<td>$A$</td>
<td>$(E_{\eta}-E_{\lambda})$</td>
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<tr>
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<tr>
<td>Na$^+$</td>
<td>3.6257</td>
<td>-4815</td>
<td>-0.5007</td>
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</tr>
<tr>
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</tr>
<tr>
<td>K$^+$</td>
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<td>-0.6348</td>
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<tr>
<td>Cs$^+$</td>
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<td>-0.6007</td>
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<tr>
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<tr>
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<tr>
<td>I$^-</td>
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<td>-4766</td>
<td>-0.4419</td>
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Table 3-6 Standard relative error and standard deviation for prospective limiting ionic conductivity fitting equations for several ions in H$_2$O and D$_2$O.

<table>
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<th>Ion</th>
<th>H$_2$O</th>
<th>D$_2$O</th>
</tr>
</thead>
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<tr>
<td>Cl$^-$</td>
<td>0.00529</td>
<td>0.00369</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.07270</td>
<td>0.06074</td>
</tr>
<tr>
<td>Na$^+$</td>
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<td>0.00559</td>
</tr>
<tr>
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<tr>
<td>K$^+$</td>
<td>0.00529</td>
<td>0.00369</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.07270</td>
<td>0.06074</td>
</tr>
<tr>
<td>Cs$^+$</td>
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<td>0.00237</td>
</tr>
<tr>
<td>Cs$^+$</td>
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<td>0.04870</td>
</tr>
<tr>
<td>I$^-$</td>
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<td>0.00142</td>
</tr>
<tr>
<td>I$^-$</td>
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<td>0.03765</td>
</tr>
<tr>
<td>Average</td>
<td>0.00422</td>
<td>0.00097</td>
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</tbody>
</table>

<table>
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<th></th>
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<tr>
<td>Std. Rel Error</td>
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<td>0.00092</td>
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<td>Std. Dev.</td>
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<td>0.03036</td>
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<tr>
<td>Std. Rel Error</td>
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<td>0.00062</td>
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<tr>
<td>Std. Dev.</td>
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<td>0.02889</td>
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<td>0.03553</td>
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<tr>
<td>Std. Rel Error</td>
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<td>0.00157</td>
</tr>
<tr>
<td>Std. Dev.</td>
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<td>0.02008</td>
<td>0.02138</td>
<td>0.03963</td>
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<tr>
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<tr>
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<tr>
<td>Std. Rel Error</td>
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<tr>
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<tr>
<td>Std. Rel Error</td>
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<tr>
<td>Std. Dev.</td>
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<tr>
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Equation 1.47
Equation 1.48
Equation 1.52
Equation 3.4
Table 3-7 Density ($\rho_w$), viscosity ($\eta_w$), and dielectric constant ($\varepsilon_r$) for H$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (MPa)</th>
<th>$\rho_w$ (kg m$^{-3}$)</th>
<th>$\eta_w$ (poise)</th>
<th>$\varepsilon_r$</th>
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</thead>
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Table 3-8 Density ($\rho_{D_2O}$), viscosity ($\eta_{D_2O}$), and dielectric constant ($\varepsilon_r$) for D$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (MPa)</th>
<th>$\rho_{D_2O}$ (kg·m$^{-3}$)</th>
<th>$\eta_{D_2O}$ (poise)</th>
<th>$\varepsilon_r$</th>
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Table 3-9 Walden Product Ratios for Cl\(_{(aq)}\), K\(^+\)(aq), Na\(^+\)(aq), Cs\(^+\)(aq) and I\(^-\)(aq) from \(T = 298K\) to \(T = 598K\) at \(p = 20\) MPa

<table>
<thead>
<tr>
<th>(T)</th>
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<th>Na(^+)</th>
<th>K(^+)</th>
<th>Cs(^+)(^a)</th>
<th>Cs(^+)(^b)</th>
<th>(\Gamma)</th>
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<tr>
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<td>1.01</td>
<td>1.05</td>
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<td>0.97</td>
<td>1.09</td>
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<td>1.04</td>
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<td>1.07</td>
<td>1.03</td>
<td>1.04</td>
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<tr>
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<td>1.08</td>
<td>1.02</td>
<td>1.04</td>
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</tr>
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</table>

a: from \(\Lambda^\circ\) (CsCl)
b: from \(\Lambda^\circ\) (CsI)
Figure 3.1 Experimental equivalent conductivity of aqueous NaCl(■), KCl(Δ), CsCl(◊), KI(○), and CsI(□) in H₂O from T = 298 K to 598 K at p = 20 MPa: solid line, Equation 1.52.
Figure 3.2 Experimental equivalent conductivity of aqueous NaCl(■), KCl(△), CsCl(◊), KI(○), and CsI(□) in D_2O from T = 298 K to 598 K at p = 20 MPa: solid line, Equation 1.52.
Figure 3.3: Plot of $\log_{10}(t^°_{\text{Cl}^-}/t^°_{\text{Na}^+})$ vs $1000/T$ for literature NaCl transference numbers in H$_2$O and D$_2$O (Longsworth, 1932; Allgood and Gordon, 1942; Smith and Dismukes, 1964; Swain and Evans, 1966)
Figure 3.4 Plot of \( \log_{10}(t_{Cl^-}/t_{K^+}) \) vs 1000/T for literature KCl transference numbers in H\textsubscript{2}O and D\textsubscript{2}O (MacInnes and Longsworth, 1932; Allgood \textit{et al.}, 1940; Smith and Dismukes, 1963; Nakahara \textit{et al.}, 1985).
Figure 3.5 $t_+^o$ and $t_-^o$ values for Na$^+$ and Cl$^-$ in H$_2$O and D$_2$O (Longsworth, 1932; Allgood and Gordon, 1942; Smith and Dismukes, 1963; Swain and Evans, 1966).
Figure 3.6 $t_\circ^+$ and $t_\circ^-$ values for K$^+$ and Cl$^-$ in H$_2$O and D$_2$O (MacInnes and Longsworth, 1932; Allgood et al., 1940; Smith and Dismukes; 1964, Nakahara et al., 1985)
Figure 3.7 Values for experimental limiting conductivity for Cl$^-$ in H$_2$O at infinite dilution as a function of temperature split using extrapolated transference numbers. (□) NaCl this study, (Δ) KCl this study, (■) NaCl Ho et al. (1994) (▲) KCl Ho et al. (2000), solid line, Zimmerman et al. (2012).
Figure 3.8 Experimental equivalent conductivity of aqueous Na$^+$ (∆), K$^+$ (●), Cl$^-$ (■), Cs$^+$ (◇), and I$^-$ (○) in H$_2$O from $T = 298$ K to 598 K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 3.9 Experimental equivalent conductivity of aqueous Na⁺(Δ), K⁺(●), Cl⁻(■), Cs⁺(◇), and I⁻(○) in D₂O from T = 298 K to 598 K at p = 20 MPa: solid line, Equation 1.52.
Figure 3.10 Plots of relative error for limiting ionic conductivity fitting equations as a function of $T$ (●) Brummer and Hills (1961), (■) Smolyakov (1968), (▲) Zimmerman et al. (2012) and (♦) the empirical function (Equation 3.4) in H$_2$O
Figure 3.11 Plots of relative error for limiting ionic conductivity fitting equations as a function of $T$ (●) Brummer and Hills (1961), (■) Smolyakov (1968), (▲) Zimmerman et al. (2012) and (♦) the empirical function (Equation 3.4) in D$_2$O.
Figure 3.12 Plot of ($R_{Walden}^{T/298K}$) / ($R_{Walden}$ at $T = 298K$) for aqueous $\text{Na}^{+} (\Delta), \text{K}^{+} (\bullet), \text{Cl}^{-} (\blacksquare), \text{Cs}^{+} (\diamondsuit)$, and $\Gamma (\circ)$ in $\text{H}_2\text{O}$ from $T = 298\text{ K}$ to $598\text{ K}$ at $p = 20\text{ MPa}$: solid line, fit by equation 1.52.
Figure 3.12 Walden Product Ratio of aqueous Cl(■), I(○), and Cs⁺(◊) from $T = 298$ K to $598$ K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 3.14 Walden Product Ratio of aqueous Na\(^+\)(\(\bigtriangleup\)) and K\(^+\)(\(\blacklozenge\)) from \(T = 298\) K to 598 K at \(p = 20\) MPa: solid line, Equation 1.52.
Chapter 4 Limiting Conductivities of Acids and Bases in H$_2$O and D$_2$O

4.1 Introduction

Presented in this chapter is the limiting molar conductivity $\Lambda^\circ$ measurements conducted on proton and hydroxide bearing solutions in light and heavy water from $T = 298$ K to 598 K and at $p = 20$ MPa. These measurements were conducted using the flow AC conductimeter and experimental design presented in Chapter 2.

Limiting ionic conductivities have been calculated using values of $\lambda^\circ$ (Cl$^-$) derived from the transference numbers from Smith and Dismukes (1963, 1964) extrapolated to the experimental conditions that were presented in Chapter 3. The assumption used to estimate transference numbers in D$_2$O was discussed in Section 3.3. The fitting of theoretical conductivity models to the experimental limiting ionic conductivity data resulted in a clear choice for the most suitable model.

In this chapter we present the values for $\lambda^\circ$(H$^+$), $\lambda^\circ$(D$^+$), $\lambda^\circ$(OH$^-$) and $\lambda^\circ$(OD$^-$) from 298 to 598 K at $p = 20$ MPa. The Walden product ratios for the deuteron/proton and deuteroxide/hydroxide have been calculated, which show a clear difference in ionic movement between light and heavy water. This difference is the contribution to the ionic movement related to proton hopping, which has been determined using the method of Tada et al. (1992, 1993).
4.2 Limiting Molar Conductivities $\Lambda^o$

Experimental results for HCl, KOH, and NaOH in H$_2$O and DCl, and NaCl, KCl, DCl, KOD, and NaOD in D$_2$O are tabulated in Table 4.1 and Table 4.2, respectively, together with the values from NaCl and KCl from Chapter 3. As was done in Section 3.1, the concentrations are tabulated both as molarities, $c = \text{mol of solute} \cdot \text{L}^{-1}$, and in molalities, $m = \text{mol of solute} \cdot \text{kg}^{-1}$, along with the specific conductivity, $\kappa$, and the corresponding molar conductivity, $\Lambda^{\exp}$.

The limiting molar conductivities, $\Lambda^o$ of each species were also calculated using the FHFP equation as described in Section 1.5.2. Values of $\Lambda^o$ are listed in Tables 4.1 and 4.2 and plotted as a function of temperature in Figure 4. (H$_2$O) and Figure 4. (D$_2$O). The plots show an increase in conductivity with temperature for all solutions, though the increase in conductivity is not linear for the proton/deuteron and hydroxide/deuteroxide solutions.

The solid line is the fit of Equation 1.52 to the data. The other three modelling equations (Equations 1.47, 1.48 and 3.4) that were considered in Section 3.1 were unable to be fitted highly curved plots of $\lambda^o$ vs $T$ for proton/deuteron and hydroxide/deuteroxide solutions. Unlike the binary salts studied in Chapter 3, all three parameters of Equation 1.52 were required to fit the experimental data, showing that molar conductivity of the proton and deuteron containing solutions is dependent on both the viscosity and the density of the solvent.
4.3 Single Ion Conductivity $\lambda^o$

The single ion conductivities, $\lambda^o$ of Cl$^-$, K$^+$, Na$^+$, H$^+$ and OH$^-$, in H$_2$O and Cl$^-$, K$^+$, Na$^+$, D$^+$ and OD$^-$ in D$_2$O are tabulated in Table 4-3 and Table 4-4, respectively. These values were calculated from $\Lambda^o$ using extrapolated values of $\lambda^o$ (Cl$^-$) derived from the work of Smith and Dismukes (1963,1964) that were presented explained in Section 3.3. To split the molar conductivities of the solutions in D$_2$O into individual ionic contributions we calculated values of $t^o$ from Equation 1.15 used the coefficients tabulated in Table 1-1.

Limiting ionic conductivities are plotted as a function of temperature in Figure 4. (H$_2$O) and Figure 4. (D$_2$O). The values of $\lambda^o$ for sodium, potassium and chloride ions were reported in the previous section and were included here for reasons that will be discussed in Section 4.4 The conductivities of the OH$^-$ ion and OD$^-$ ion increase across the experimental temperature range, though the increase is not strictly linear. For the H$^+$ and D$^+$ ions, the conductivity reaches a maximum value at $T = 523$ K for the proton and $T = 548$ K for the deuteron. The proton and deuteron have greater conductivity at lower temperatures, but are overtaken by the hydroxide and deuteroxide at $\sim T = 573$ K and 598 K respectively.

The solid curves indicate our fits of Equation 1.52 to the experimental limiting ionic conductivities. The fitting parameters for the ions are tabulated in Table 4-5. All three fitting parameters were required in order to fit the model to the experimental data, meaning that both the density and the viscosity of the solvent are required to determine the conductivity of the hydrogen and deuterium containing ions.
4.4 Walden Product Ratios

The Walden product ratios for the ions, $R_{Walden}^{D/H}$, are tabulated in Table 4-6. Plots of the Walden product ratio over the experimental temperature range are shown in Figure 4.5. The solid curve is the fit of Equation 1.52 to the experimental data. The trends observed for the proton/deuteron and hydroxide/deuteroxide differ significantly from the alkali metals and halides in Section 3.4, as both have Walden product ratio values less than 1, indicating more efficient transport in light water than heavy water. For the deuteron/proton, the ratio is relatively independent of temperature over the entire range of experimental conditions whereas the deuteroxide/hydroxide appears to be heavily favour light water transport at ambient conditions, decreasing the difference between the mechanism of ionic transport as the temperature increases before levelling out above ~ 548K.

4.5 Proton Hopping

The significant difference in the temperature dependence of $\lambda^\circ$ and the Walden product ratio for the proton/deuteron and hydroxide/deuteroxide relative to the alkali metal and halide ions is due to proton hopping. As discussed in Section 1.5.7, hydrogen and hydroxide ions and their deuterated counterparts move through solution by two mechanisms, i.e. by diffusion through the bulk solvent (the same method as other ions) or through proton hopping as shown in Figure 1.9.

To determine the excess limiting ionic conductivity, $\lambda_{E}^\circ$ arising from proton hopping, we adopted the method used by Tada et al. (1992,1993) who postulated that the
bulk movement of the proton (in this case represented as an H$_3$O$^+$ ion) and hydroxide can be assumed to be the same as K$^+$ and Cl$^-$ ions respectively, as they have similar ionic radii. Thus, by subtracting the bulk contribution (i.e. $\lambda^0$ of K$^+$ or Cl$^-$) from the total experimental value of H$_3$O$^+$ or OH$^-$, we can obtain the value for $\lambda_{E}^0$, the “excess” ionic conductivity that arises from proton hopping:

$$\lambda_{E}^0 (H^+) = \lambda^0 (H^+) - \lambda^0 (K^+) \quad (4.1)$$

$$\lambda_{E}^0 (OH^-) = \lambda^0 (OH^-) - \lambda^0 (Cl^-) \quad (4.2)$$

The values for the excess proton conductivity are tabulated in Table 4-7 for H$_2$O and Table 4-8 for D$_2$O. Plots of limiting conductivity versus temperature which illustrate the trends in total conductivity, the individual contribution from the bulk sphere movement and from proton hopping are given in Figure 4-6 through Figure 4.9.

These figures indicate that the contribution to the experimental conductivity due to proton hopping is greatest at ambient temperatures and falls off towards hydrothermal conditions. Figure 4.10 shows excess conductivity arising from proton hopping for H$_3$O$^+$, OH$^-$, D$_3$O$^+$, and OD$^-$ as a function of temperature. At ambient conditions, proton hopping in H$_3$O$^+$ is heavily favoured, followed by D$_3$O$^+$ and OH$^-$, while the contribution for OD$^-$ is lowest. Proton hopping for the H$_3$O$^+$ and D$_3$O$^+$ reach maxima at $T$=423K and their contribution to the total conductivity greatly diminishes towards the end of the experimental temperature range. The proton hopping for OH$^-$ and OD$^-$ reaches maxima at $T$=523K, but the contribution to total conductivity does not diminish as quickly as for H$_3$O$^+$ and D$_3$O$^+$.  

Figure 4.11 shows the ratio of the excess conductivity as a fraction of the total conductivity over the experimental temperature range. At ambient temperatures, the
proton hopping of H$_3$O$^+$ makes up 77% of the total conductivity, with the ratios for D$_3$O$^+$, OH$^-$ and OD$^-$ being 72%, 61% and 38%. This compares favourably to the work of Tada et al., (1992, 1993) whose reported values at 298 K lead to contributions of 79%, 74%, 62% and 46% respectively. At $T = 598$ K, the ratio of proton hopping to the total conductivity for H$_3$O$^+$ has fallen to 36%, with values of 35%, 27% and 20% for OH$^-$, D$_3$O$^+$, and OD$^-$ respectively. The work of Tada et al, (1992, 1993) only reached temperatures of 338 K, thus values beyond that temperature reported here are the first ever reported.

The $R_{Walden}^{D/H}$ plot for the proton hopping contributions is shown in Figure 4. The deuteron/proton plot shows that proton hopping in light water is favoured across the temperature range becoming even more favoured at $T = 598$ K. The deuteroxide/hydroxide plot shows an ever greater affinity for proton hopping in light water at ambient temperatures, though it decreases slightly at higher temperatures before again becoming more favoured as the critical point approaches.

4.6 Discussion

The excess limiting ionic conductivity arising from proton hopping shown in Figures 4.3 and 4.4 is the cause of the ‘bowing’ trend in the limiting ionic conductivities for H$^+$, D$^+$, OH$^-$ and OD$^-$ across the experimental temperature range. The contribution to total conductivity from proton hopping is the cause of the maximum values for ionic conductivity of H$^+$ and D$^+$, although we surmise that it may only be a local maximum, as the conductivity of the bulk sphere should overtake the maximum the reported maximum value at elevated temperatures. As the contribution due to proton hopping for the OH$^-$ and OD$^-$ ions is less than that observed for H$^+$ and D$^+$, there is not an observed maximum
value in the temperature range, as the bulk sphere ionic movement is the major contributor to the observed ionic movement.

The deuterated ions in solution are less favoured for proton hopping compared to their protonated analogues. This effect is largely due to reduced mass of a D$_2$O molecule compared to an H$_2$O molecule (McQuarrie and Simon, 1997). As discussed in section 1.3, the hydrogen bonding in heavy water is approximately 25% stronger than that of light water (Hill, 1982). Thus the requirement of breaking these hydrogen bonds for the purpose of proton hopping requires a greater energy investment. Furthermore, the energy used to rotate a deuterium atom is greater than that of a hydrogen atom owing to the reduced mass, causing the proton hopping process to be less energetically favourable.

The maxima observed for the proton hopping contribution to the limiting ionic conductivity for H$^+$ and D$^+$ is due to two converging factors. As the temperature increases, the thermal energy in the system cause the rotation of the molecules in solution to become more favourable (Tada et al., 1992), assisting in the proton hopping process and causing an increase in conductivity. However, the other consequence of the increasing temperature is a decrease in the coordination number of each water molecule (Balbuena et al., 1996), resulting in fewer neighbouring water molecules to act as proton acceptors. Additionally, as the viscosity of the solution decreases, bulk ionic movement will become less constrained, resulting in the decrease in the contribution of proton hopping to the total ionic movement.

The above physical factors cause the proton hopping contribution [i.e. $\lambda^\circ_E (H^+) / \lambda^\circ (H^+)$] to be greatest at ambient conditions while the conductivity goes through a maximum value at $T = 423$ K, which is striking because this is the temperature where the
tetrahedral orientation of hydrogen bonding breaks down and the solvent becomes more continuum-like (Seward and Driesner, 2004). This would indicate that the magnitude of the proton hopping mechanism is due to the pre-rotation of molecules, which is dependent on neighbouring solvent molecules (Tada et al., 1994). The solvent molecules surrounding the \( \text{H}_3\text{O}^+ \) molecule maintain a tetrahedral configuration at lower temperature, which forces the pre-rotation of one of the neighbouring water molecules, caused by the repulsive force between hydrogen atoms. As the temperature increases, the number of coordinating solvent molecules decreases, and pre-rotation of neighbouring molecules is less favoured. The excess proton on the \( \text{H}_3\text{O}^+ \) ion can settle into an uncoordinated position, which eliminates the pre-rotation due to the repulsive force and significantly decreases the extent of proton hopping within the solution (Tada et al., 1994).

The lower contribution of proton hopping in the \( \text{OH}^- \) and \( \text{OD}^- \) is due to the repulsive effect between the \( \text{OH}^- \) and neighbouring water (HOH) molecules being relatively small (Tada et al., 1993) compared to the repulsive effect observed for \( \text{H}^+ \) and \( \text{D}^+ \). This means that the hydroxide and deuteroxide compounds, the rotation of neighbouring water molecules is the rate limiting step for proton hopping and the reason why the maxima is reached at a greater temperature. The increased rotation caused by the thermal energy counters the lowering of coordinated solvent molecules and decrease in viscosity, resulting in a maximum value that occurs at a higher temperature of \( T = 523 \text{K} \).

The maximum occurring at a higher temperature for \( \text{OH}^- \) and \( \text{OD}^- \) compared to \( \text{H}^+ \) and \( \text{D}^+ \) shows that it is the pre-rotation of the latter at ambient temperatures that is the largest contributor to the greater values of \( \lambda_{\text{E}}^o \) observed for \( \text{H}^+ \) and \( \text{D}^+ \) from 298 K to 423
K. At $T = 423$ K, the pre-rotation is significantly less favoured due to a decrease in the coordination number of the solvent, resulting in a sharp decrease in $\lambda^o_E$ as the temperature increases. For the hydroxide and deuteroxide, once the solvent species has lost its tetrahedral orientation at $T = 423$ K, value of $\lambda^o_E$ continues to increase, showing that proton hopping for these ions is largely as a result of thermal energy rotating neighbouring solvent molecules. As the number of coordinated solvent molecule decreases, it is likely that thermal energy will drive both proton hopping process, and the excess conductivity for all proton hopping species in their respective solvents will be at parity [i.e.. $\lambda^o_E(\text{H}^+) = \lambda^o_E(\text{OH}^-)$ at high $T$]

Comparing the ratios of excess conductivities in light water versus heavy water to those reported by Tada et al. (1992, 1993) at $T = 298$K, shows good agreement. Our reported value for the ratio $\lambda^o_E(\text{H}^+) / \lambda^o_E(\text{D}^+)$ is 1.51, while Tada’s value is 1.47. The experimental value for $\lambda^o_E(\text{OH}^-) / \lambda^o_E(\text{OD}^-)$ is 2.94 versus 2.27 from the literature. This discrepancy is due to small deviations between the literature and experimental values for $\lambda^o(\text{Cl}^-)$ and $\lambda^o(\text{OH}^-)$ of less than $\pm 10$ S·cm·mol$^{-1}$. In general, this relationship is poor at determining the effect of solvent on proton hopping as it doesn’t account for differences in the solvent viscosity or density between H$_2$O and D$_2$O.

The Walden product ratio is a much better method for comparing the conductivity divergences caused by differing reduced mass and hydrogen bonding between the two solvents. For the comparison of D$^+$/H$^+$ as seen in Figure 4.11, the value for $R_{\text{Walden}}^{\text{D/H}}$ stays constant throughout the temperature range though it does trend up slightly at higher temperatures. This indicates that the transfer of protons is favoured in light water, which is mostly due to the difference in proton hopping elaborated on above. For the OD$^-$/OH$^-$
ratio, at ambient temperatures the transport of OH$^-$ is highly favoured, becoming less so as the temperature increases. This difference in largely due to the relative strength of hydrogen bonding in H$_2$O and D$_2$O. For a neighbouring solvent molecule to rotate, it must break two hydrogen bonds (Tada et al., 2004). As the hydrogen bonds at low temperature are known to be stronger in D$_2$O than H$_2$O, the amount of energy required to break these bonds will be greater in D$_2$O, leading to less favoured proton hopping. As the temperature increases and hydrogen bonding decreases, this solvent effect is diminished. This effect is less noticeable for D$^+/H^+$ as the repulsive forces between the proton and the hydrogen atom of a water molecule are enough to break the hydrogen bond in both H$_2$O and D$_2$O, causing the pre-rotation which is required for proton hopping.

The $R_{\text{Walden}}^{\text{D}/\text{H}}$ values of the excess conductivity for D$^+/H^+$ indicate that contribution for proton hopping remains appropriately constant for over the experimental temperature range as shown in Figure 4.12. Hopping is shown to always be favoured in light water solutions, mostly due to the reduced mass of the ions as discussed above. The $\sqrt{2}$ relationship proposed by Tada et al. (1992, 1994) for the excess conductivities in light and heavy water taken from the reduced mass doesn’t hold true when the conductivities have been corrected using the solvent viscosity. $R_{\text{Walden}}^{\text{D}/\text{H}}$ for OD$^-$/OH$^-$ as a function of temperature indicates a very large preference for the hopping of OH$^-$. The hopping mechanism for OD$^-$ becomes slightly more favourable as temperature increases due to an increase in thermal energy, but across the entire temperature region, the contribution to ionic movement from OH$^-$ is twice that of OD$^-$. 

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Table 4-1: Values of Experimental Molar Conductivities, $\Lambda_{\text{exp}}$, and Fitted Limiting Molar Conductivities, $\Lambda^\circ$, for NaCl(aq), KCl(aq), HCl(aq), NaOH(aq), and KOH(aq) in H$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

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<th>$\kappa \times 10^6$ (S cm$^{-1}$)</th>
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<td>842.99</td>
<td>748.19</td>
<td>819.96</td>
<td>860.56 ± 8.61</td>
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<tr>
<td>DCl (aq)</td>
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<td>813.11</td>
<td>1030.99</td>
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<td>NaOD (aq)</td>
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<td>1226.05</td>
<td>920.17</td>
<td>961.10 ± 9.61</td>
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<tr>
<td>KOD (aq)</td>
<td>807.80</td>
<td>630.10</td>
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<td>967.65</td>
<td>1003.55 ± 10.04</td>
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<td>NaCl (aq)</td>
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<td>642.92</td>
<td>838.25</td>
<td>877.93 ± 8.78</td>
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<td>906.68</td>
<td>873.75</td>
<td>918.95 ± 9.19</td>
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<tr>
<td>DCl (aq)</td>
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<td>957.78</td>
<td>1115.25</td>
<td>1156.96 ± 11.57</td>
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<td>NaOD (aq)</td>
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<td>NaCl (aq)</td>
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<td>950.83 ± 9.51</td>
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<td>NaOD (aq)</td>
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<td>992.49</td>
<td>1011.95</td>
<td>1064.04 ± 10.64</td>
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<td>1106.08 ± 11.06</td>
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Table 4-21 Values of Experimental Molar Conductivities, $Λ_{\text{exp}}$, and Fitted Limiting Molar Conductivities, $Λ^*$, for NaCl(aq), KCl(aq), DCl(aq), NaOD(aq), and KOD(aq) in D$_2$O from $T=298$ K to $T=598$ K at $p=20$ MPa.
Table 4-3 Values of Limiting Ionic Conductivities, $\lambda^o$, for Cl$_{(aq)}^-$, K$^+(aq)$, Na$^+(aq)$, H$^+(aq)$, and OH$^-_{(aq)}$ in H$_2$O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

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<tr>
<th>$T$ (K)</th>
<th>$t^o_{CL}$</th>
<th>$\lambda^o(Cl^-)$</th>
<th>$\lambda^o(Na^+)$</th>
<th>$\lambda^o(K^+)$</th>
<th>$\lambda^o(H^+)$</th>
<th>$\lambda^o(OH^-)$</th>
<th>$\delta\lambda^o/\lambda^o$</th>
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</thead>
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<tr>
<td>298.162</td>
<td>0.5095</td>
<td>83.29</td>
<td>56.03</td>
<td>80.18</td>
<td>353.34</td>
<td>213.22</td>
<td>±0.010</td>
</tr>
<tr>
<td>373.150</td>
<td>0.5195</td>
<td>205.69</td>
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<td>190.27</td>
<td>636.81</td>
<td>437.49</td>
<td>±0.014</td>
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<tr>
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<td>±0.010</td>
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<td>799.01</td>
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<td>±0.014</td>
</tr>
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<td>0.5308</td>
<td>471.36</td>
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<td>416.67</td>
<td>828.88</td>
<td>731.04</td>
<td>±0.017</td>
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<td>548.100</td>
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<td>432.90</td>
<td>812.71</td>
<td>745.58</td>
<td>±0.014</td>
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<td>526.68</td>
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<td>800.02</td>
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<td>±0.014</td>
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<td>488.98</td>
<td>765.48</td>
<td>772.49</td>
<td>±0.017</td>
</tr>
</tbody>
</table>

a: from $\Lambda^o$ (NaOH)
b: from $\Lambda^o$ (KOH)
c: precision relative to other ions measure in thesis
Table 4- 4: Values of Limiting Ionic Conductivities, $\lambda^{\circ}$, for Cl\(^{-}\)\textsubscript{(aq)}, K\(^{+}\)\textsubscript{(aq)}, Na\(^{+}\)\textsubscript{(aq)}, D\(^{+}\)\textsubscript{(aq)}, and OD\(^{-}\)\textsubscript{(aq)}, in D\(_2\)O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa

<table>
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<th>$T$ (K)</th>
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<th>$\lambda^{\circ}(\text{Cl}^{-})$</th>
<th>$\lambda^{\circ}(\text{Na}^{+})$</th>
<th>$\lambda^{\circ}(\text{K}^{+})$</th>
<th>$\lambda^{\circ}(\text{D}^{+})$</th>
<th>$\lambda^{\circ}(\text{OH})$(^ a )</th>
<th>$\lambda^{\circ}(\text{OH})$(^ b )</th>
</tr>
</thead>
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<td>70.78</td>
<td>251.16</td>
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<td>399.70</td>
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<td>663.50</td>
<td>577.90</td>
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<tr>
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<td>406.97</td>
<td>696.23</td>
<td>602.21</td>
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<tr>
<td>572.800</td>
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<td>392.50</td>
<td>433.52</td>
<td>671.53</td>
<td>630.89</td>
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<td>631.09</td>
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$\delta \lambda^{\circ}/\lambda^{\circ}$\(^ c \) $\pm 0.010$ $\pm 0.014$ $\pm 0.010$ $\pm 0.014$ $\pm 0.017$ $\pm 0.014$

$\text{a: from} \quad \Lambda^{\circ} (\text{NaOH})$

$\text{b: from} \quad \Lambda^{\circ} (\text{KOH})$

$\text{c: precision relative to other ions measure in thesis}$
Table 4- 5 Fitting parameters for H⁺, D⁺, OH⁻ and OD⁻ for fitting equation 1.52 (Zimmerman et al. 2012)

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<tr>
<th>Species</th>
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<td></td>
<td>A₁</td>
</tr>
<tr>
<td>H⁺</td>
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</tr>
<tr>
<td>D⁺</td>
<td>1.4033</td>
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<tr>
<td>OH⁻</td>
<td>-0.7191</td>
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<tr>
<td>OD⁻</td>
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Table 4-6: Walden Product Ratios for Cl, Na⁺, K⁺, D⁺/H⁺, OD⁻/OH⁻, D⁺/H⁺, and OD⁻/OH⁻ from $T = 298K$ to $T = 598K$ at $p=20$ MPa

<table>
<thead>
<tr>
<th>$T$</th>
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<th>Na⁺</th>
<th>K⁺</th>
<th>H⁺</th>
<th>OH⁻ a</th>
<th>OH⁻ b</th>
<th>$\lambda_E^\circ (H^+)$</th>
<th>$\lambda_E^\circ (OH^-)$</th>
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<td>0.91</td>
<td>0.83</td>
<td>0.79</td>
<td>0.58</td>
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<td>1.00</td>
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<td>0.89</td>
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a: from $\Lambda^\circ$ (NaOH)
b: from $\Lambda^\circ$ (KOH)
Table 4- 7 Values of Limiting Ionic Conductivities, \( \lambda^\circ \), for Cl\(^-\)(aq), K\(^+\)(aq), H\(^+\)(aq), OH\(^-\)(aq), H\(^+\)_E and OH\(^-\)_E in H\(_2\)O from \( T = 298 \) K to \( T = 598 \) K at \( p = 20 \) MPa

<table>
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<th>( T ) K</th>
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<th>( \lambda^\circ(\text{Na}^+) )</th>
<th>( \lambda^\circ(\text{K}^+) )</th>
<th>( \lambda^\circ(\text{H}^+) )</th>
<th>( \lambda^\circ(\text{OH}^-) )</th>
<th>( \lambda^\circ(\text{H}^+) )</th>
<th>( \lambda^\circ(\text{OH}^-) )</th>
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\( \delta \lambda^\circ/\lambda^\circ \) a ±0.010 ±0.014 ±0.010 ±0.014 ±0.014 ±0.017 ±0.017

a: precision relative to other ions measured in thesis
Table 4- 8 Values of Limiting Ionic Conductivities, $\lambda^\circ$, for Cl$^-(aq)$, K$^+(aq)$, D$^+(aq)$, OD$^-(aq)$, D$^+\_E$ and OD$^-\_E$ in D$_2$O from $T = 298 \text{ K}$ to $T = 598 \text{ K}$ at $p = 20 \text{ MPa}$

<table>
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<th>$T$ (K)</th>
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<th>$\lambda^\circ(\text{Na}^+)$</th>
<th>$\lambda^\circ(\text{K}^+)$</th>
<th>$\lambda^\circ(\text{D}^+)$</th>
<th>$\lambda^\circ(\text{OD}^-)$</th>
<th>$\lambda^\circ(E)(\text{D}^+)$</th>
<th>$\lambda^\circ(E)(\text{OD}^-)$</th>
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<td>289.26</td>
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<td>645.34</td>
<td>170.34</td>
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$\delta\lambda^\circ/\lambda^\circ$\(^a\) ±0.010 ±0.014 ±0.010 ±0.014 ±0.014 ±0.017 ±0.017

\(^a\) precision relative to other ions measured in thesis
Figure 4.1 Limiting molar conductivity of aqueous NaCl(■), KCl(Δ), NaOH(▲), KOH(♦) and HCl(●) in H₂O from T = 298 K to 598 K at p = 20 MPa: solid line, Equation 1.52.
Figure 4.2: Limiting molar conductivity of aqueous NaCl(■), KCl(▲), NaOD(▲), KOD(♦) and DCl(●) in D₂O from $T = 298$ K to $T = 598$ K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 4.3: Limiting ionic conductivity of aqueous Na$^+$ (Δ), K$^+$ (●), Cl$^-$ (■), H$^+$ (○), and OH$^-$ (▲) in H$_2$O from $T = 298$ K to 598 K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 4.4: Limiting ionic conductivity of aqueous Na\(^+\) (Δ), K\(^+\) (●), Cl\(^-\) (■), D\(^+\) (●), and OD\(^-\) (▲) in D\(_2\)O from \(T = 298\) K to 598 K at \(p = 20\) MPa: solid line, Equation 1.52.
Figure 4. 5 Walden Product Ratio of aqueous $D^+/H^-(\bullet)^-$ and OD$^-$/OH$(\Delta)$ from $T = 298$ K to 598 K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 4.6 Limiting ionic conductivity for $\text{H}_3\text{O}^+$ (●), separated into diffusion (○) and proton hopping (♦) contributions in H$_2$O from $T = 298$ K to 598 K at $p = 20$ MPa: solid line, Equation 1.52.
Figure 4.7 Limiting ionic conductivity for $\text{D}_3\text{O}^{+}(\bullet)$, separated into diffusion (○) and proton hopping (♦) contributions in D$_2$O from $T = 298$ K to 598 K at $p = 20$ MPa; solid line, Equation 1.52.
Figure 4.8 Limiting ionic conductivity for $\text{OH}^-$ ($\blacktriangle$), separated into diffusion ($\Delta$) and proton hopping ($\blacksquare$) contributions in $\text{H}_2\text{O}$ from $T = 298$ K to 598 K at $p = 20$ MPa; solid line, Equation 1.52.
Figure 4. 9 Limiting ionic conductivity for OD\(^{\circ}(\Delta)\), separated into diffusion (Δ) and proton hopping (■) contributions in D\(_2\)O from \(T = 298\) K to 598 K at \(p = 20\) MPa; solid line, Equation 1.52.
Figure 4. 10 Limiting ionic conductivity arising from proton hopping for $\text{H}^+(\circ)$, $\text{D}^+(\bullet)$, $\text{OH}^-(\square)$ and $\text{OD}^- (\blacksquare)$ from $T = 298$ K to 598 K at $p = 20$ MPa; solid line, Equation 1.52.
Figure 4.11 Ratio of proton hopping contributions to conductivity versus total conductivity of for H$^+$ (○), D$^+$ (●), OH$^-$ (□) and OD$^-$ (■) from $T = 298$ K to 598 K at $p = 20$ MPa: The solid curve is the fit to Equation 1.52.
Figure 4. 12: Walden Product Ratio of proton hopping contributions for aqueous $\text{D}^+$/H$^+$ (●) and OD$^-$/OH$^-$ (■) from $T = 298$ K to 598 K at $p = 20$ MPa: solid line, Equation 1.52.
Chapter 5 Conclusions and Future Topics

5.1 Limiting Conductivities

Values of $\Lambda^\circ$ were measured for a variety of binary salts, hydrochloric acid, potassium and sodium hydroxide in light and heavy water, which were reported in Chapters 3 and 4. These values were used to determine limiting ionic contributions for each ion using literature values for transference numbers extrapolated to high temperature. This extrapolation proved to be accurate for transference numbers of both NaCl and KCl, from which values of $\lambda^\circ(\text{Cl}^-)$ were determined which agreed very well to both literature values and the fit of all Cl$^-$ data from Zimmerman et al. (2012.)

5.2 Ionic Transport and Hydration

Values for $\lambda^\circ$ determined from transference numbers across the experimental temperature range followed model for temperature dependence of ionic mobilities first proposed by Frank and Wen (1957). The conductivity of “structure-breaking” ions K$^+$, Cs$^+$, Cl$^-$, and I$^-$ was enhanced at low temperatures compared to that at high temperature. In addition their structure breaking properties improved the transport of K$^+$, Cs$^+$, and Cl$^-$ at low temperatures in heavy water versus light water, due to the more deuterated solvent being more structured at ambient temperatures.

Comparison of the ionic transport using the Walden product ratio indicated that there is minimal solvent isotope effect, particularly at high temperatures. The difference
in conductivities for ions in light and heavy water at the same temperature is due to the disparity in viscosity between the two solvents.

5.3 Proton Hopping

The contribution ionic conductivity from proton hopping for ions in light and heavy water was determined for the first time above 318 K. Proton hopping for the H\textsuperscript{+} and D\textsuperscript{+} ions is highly favoured at low temperatures where the pre-rotation of adjacent water molecules facilitates the hopping process. As the temperature increases and the tetrahedral hydrogen bonded structure of water breaks down (above 423 K) proton hopping is significantly less favoured as a mechanism for ionic transport. The limiting ionic conductivity arising from proton hopping in OH\textsuperscript{-} and OD\textsuperscript{-} solutions increases across the temperature range, as the proton hopping mechanism is dependent on the thermal energy in the solution providing the rotation necessary to begin the proton hopping step. At the end of the experimental temperature range (T = 598 K), the proton hopping mechanism is almost completely driven by the thermal energy in solution, causing the excess conductivity for H\textsuperscript{+} and OH\textsuperscript{-} as well as D\textsuperscript{+} and OD\textsuperscript{-} to approach parity.

The $R_{Walden}^{D/H}$ values across the temperature range show that there is little change in the ratio of excess conductivity for D\textsuperscript{+} and H\textsuperscript{+}, with the excess conductivity being 1.25 times great in for H\textsuperscript{+} ions. The ratio for OH\textsuperscript{-} and OD\textsuperscript{-} shows that the proton hopping in hydroxide solutions contributes twice as much as for the deuterated species.
5.4 Future Topics

The work presented in this thesis is a good basis for conductivity measurements of ions in light and heavy water. In the future, extending the experimental temperature range through the critical point to the limits of the conductimeter \( T = 400 \text{ K} \) would give insight regarding the effect that rapidly changing physical properties would have on the ionic conductivity. In addition, measurements of the conductivity of \( \text{H}^+, \text{D}^+, \text{OH}^- \) and \( \text{OD}^- \) would provide a full understanding of the effect of solvent coordination to the excess conductivity arising from proton hopping. Furthermore, experiments into the critical point range would test our transference number extrapolation, as Figure 3.7 indicated that it was suitable for literature values of conductivity close to the critical point, but faltered due to large changes in solvent properties.

Further measurements on fission product species are planned. Our group has conducted measurements on strontium solutions (2:1 electrolytes), and are planning to continue with 3:1 electrolytes, such as lanthanum. In addition, completing measurements on iodide-containing salts which are not harmful to the operation of the cell are a possibility given the proper experimental design.
Chapter 6 Bibliography


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