High Temperature D₂O Isotope Effects on Hydrolysis and Ionization Equilibria in Water

by

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A Thesis
Presented to
The University of Guelph

In partial fulfillment of requirements
for the degree of
Doctorate of Philosophy
in
Chemistry

Guelph, Ontario, Canada

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ABSTRACT

HIGH TEMPERATURE D₂O ISOTOPE EFFECTS ON HYDROLYSIS AND IONIZATION EQUILIBRIA IN WATER

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This thesis is an investigation of the relative differences of acid ionization constants and ion mobility in D₂O versus H₂O under hydrothermal conditions, for acetic acid and phosphoric acid. Values of specific conductivity were measured for each acid in H₂O and D₂O, as well as for a series of strong electrolytes using a high-temperature high-pressure AC conductivity flow cell that was originally designed at the University of Delaware. The Fuoss-Hsai-Fernández-Prini (FHFP) equation was fitted to the experimental values of molar conductivity, Λ, to obtain molar conductivities at infinite dilution, Λ⁰. The molar conductivities at infinite dilution for each acid were used to calculate degrees of dissociation and ionization constants in D₂O versus H₂O from 298 K to 571 K. Measured values of differences in pKₐq in D₂O vs H₂O, ΔpKₐq = [pKₐq,D₂O – pKₐq,H₂O], become relatively independent of temperature above 423 K, with values of: ΔpKₐq ≈ 0.45 for acetic acid and ΔpKₐq ≈ 0.35 for phosphoric acid. The Density Model
was then fitted to the values of $pK_{aq}$ in $H_2O$ and $D_2O$ to represent their temperature dependence to a precision of ± 0.01 in $\Delta pK_{aq}$.

Comparisons of the molar conductivities and ionic molar conductivities at infinite dilution for the strong electrolytes in $H_2O$ and $D_2O$ as a function of temperature have also been made, based on Walden’s rule correlations, $(\lambda^o \cdot \eta)_{D2O} / (\lambda^o \cdot \eta)_{H2O}$. Changes in values of $(\lambda^o \cdot \eta)_{D2O} / (\lambda^o \cdot \eta)_{H2O}$ as a function of temperature are consistent with a change in the relative hydration behavior of ions, where the effective Stokes’ radii of the ions in $D_2O$ versus $H_2O$ changes at temperatures above ~ 450 K. Changes in values of $(\lambda^o \cdot \eta)_{D2O} / (\lambda^o \cdot \eta)_{H2O}$ for $D^+/H^+$ and $OD^-/OH^-$ suggest that proton hopping “Grotthuss” mechanisms become more efficient in $D_2O$ versus $H_2O$ with increasing temperature.
For my family: All the Nygaards, Shuttleworths, and Ericksons
ACKNOWLEDGEMENTS

I would first like to thank my parents, Neil and Wanda, my brother, Jeremy, and all members of my extended family: the Nygaards, Shuttleworths and Ericksons, for all their love and support over the last 25 years of my education and their continuing support for my work in the future. I would also like to thank my friends Allison, Warren, Scott, Jennifer, my fellow Town and Gown Toastmasters (far too many to name), and my fellow Axé Mississauga Capoeira buddies (Pulga, Apretado, Hesaca, Helicoperto, Palhaco, Formigo, Gato, Scifo, Wil, Seury, Maria, Jamina, Ryan, Barb, Miguel and Natalie). Without all their help and support, I never would have made it this far, and with so many wonderful memories.

I am greatly indebted to my supervisor, Professor Peter Tremaine, who allowed me to work in his lab as a doctoral candidate on such an exciting, interesting and detailed project, and continually pushed me to reach my potential during our weekly meetings. Without his guidance and support, I surely never would have accomplished all that I have. I am also grateful for his trust in my abilities to represent his research at several international conferences in 2009, 2010, 2011 and 2012. These experiences were truly eye opening and it has been a pleasure working with Peter all this time.

Dr. Hugues Arcis and Professor Gregory Zimmerman (Bloomsburg University) also contributed a huge amount of time and effort collaborating with me on this project: developing the experimental design, making experimental conductivity measurements and interpreting the results. They both deserve a special thank you for all their hard work!
I also owe gratitude to other past and present members of Dr. Tremaine’s research group: Dr. Lilana Trevani, Dr. Melerin Madekufamba, Dr. Diego Raffa, Dr. Ephraim Bulemela, Dr. Josef Sedlbaur, Dr. Jana Ehlerova, Dr. Lucas Appelgarth, Dr. Jenny Cox, Dr. Yohann Coulier, Vanessa Mann, Rachael Diamond, Daniel Nieto, Francis Brosseau, Angeline Lam, Fransisco Ibla, Katherine Bissonette, Tiffany Fransbergen, Alexander Lowe, Jeffrey Plumridge, Michael Yacyshyn, Kevin Yin, Christopher Alcorn and Katylen McCallum for all their hard work and support. Each member contributed to the success of this thesis in their own unique way, and I never would have completed it without them.

I would like to thank my committee members, Associate Professor Daniel Thomas, Professor Paul Rowntree and Professor Terrance MacMahon (University of Waterloo) for their continuing support and assistance throughout my graduate degree. I would also like to thank Professor Serguei Lvov (Pennsylvania State University) for acting as my external examiner. Appreciation should also be given to Casey Gilien (machinist) and Ian Renaud (electrician), who helped me modify and reconstruct the high temperature and pressure conductivity cell, described in Chapter 2. They are life savers. Dr. Vassili Karanossias, Dr. Marcel Nooijen, Professor Fredrick Evers and Dr. Natasha Kenny also deserve a thank you for their enlightening courses on Analytical Chemistry, Statistical Mechanics, and Education Theory.

Finally, I could not have completed this journey without the continued help of Professor Andrew Hakin (University of Lethbridge). Andy, without you, I would have never taken this path and discovered all the possibilities that exist. Thank you.
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## LIST OF ABBREVIATIONS AND SYMBOLS

### Abbreviations

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<th>Description</th>
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<tr>
<td>A⁻</td>
<td>Anionic species</td>
</tr>
<tr>
<td>AECL</td>
<td>Atomic Energy of Canada Ltd.</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>Ac⁻</td>
<td>Acetate anion</td>
</tr>
<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
</tr>
<tr>
<td>CANDU</td>
<td>Canadian Deuterium Uranium</td>
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<td>©</td>
<td>Copyright</td>
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<tr>
<td>calc.</td>
<td>Calculated</td>
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<tr>
<td>DAc</td>
<td>Acetic acid in D₂O</td>
</tr>
<tr>
<td>est.</td>
<td>Estimated values</td>
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<tr>
<td>expt.</td>
<td>Experimental values</td>
</tr>
<tr>
<td>FHFP</td>
<td>Fuoss-Hsai-Fernández-Prini</td>
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<tr>
<td>HA</td>
<td>Weak acid</td>
</tr>
<tr>
<td>HAc</td>
<td>Acetic acid in H₂O</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
</tr>
<tr>
<td>HECC</td>
<td>Hydrogen-electrode concentration cells</td>
</tr>
<tr>
<td>HKF</td>
<td>Helgeson-Kirkham-Flowers</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-precision liquid chromatography</td>
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<tr>
<td>IAPWS</td>
<td>International Association for the Properties of Water and Steam</td>
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IP  Integrated peak
i.d.  Inner diameter (mm)
lit.  Literature values
MSA  Mean spherical approximation
o.d.  Outer diameter (mm)
PBLTR  Pressure-balanced low-temperature reference
PID  Proportional-integral-derivative
pred.  Predicted values
®  Registered trademark
RCL  Resistance capacitance inductance
RTD  Resistance temperature detector
TBBK  Turk-Blum-Bernard-Kunz
WTW  Wissenschaftlich-Technische Werkstätten
wt %  Weight percent
YSZ  Yttria-stabalized zirconia

Symbols and Variables
Å  Angstrom
$A_{DH}$  Debye-Hückel parameter
$A_M$  Debye-Hückel parameter for the Meissner equation for NaCl, equation (1.37)
$A$  Absorbance
$A_s$  Surface area of electrodes (cm$^2$)
$A_i$ (i = 1-3)  Adjustable parameters to describe $\Lambda^\circ$ as a function of $\eta_{H2O}$, equation (1.45)

$\hat{a}$  Debye-Hückel distance of closest approach

$a$  Bjerrum distance

$a_d$  Adjustable parameter for the density model, equation (1.19)

$a_{H2O}$  Activity of H$_2$O

$a_i$  Activity of ion i

$a_L$  Parameter, equation (3.13)

$B_{DH}$  Debye-Hückel parameter

$B_M$  Adjustable parameter for the Meissner equation for NaCl, equation (1.37)

$B_\gamma$  Adjustable parameter for the Pitzer equation, equation (1.35)

$B^\prime$  Adjustable parameter for the extended Debye-Hückel equation, equation (1.49)

$b_d$  Adjustable parameter for the density model, equation (1.19)

$b_L$  Parameter, equation (3.13)

$C$  Capacitance

$C_{cell}$  Cell capacitance

$C_D$  Double layer capacitance

$C_M$  Debye-Hückel parameter for the Meissner equation for NaCl, equation (1.37)

$C_p^\circ$  Partial molar heat capacity (J·K$^{-1}$·mol$^{-1}$)

$C_I$  Component of Warburg impedance

$C_\gamma$  Adjustable parameter for the Pitzer equation, equation (1.35)
<table>
<thead>
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<td>( C' )</td>
<td>Adjustable parameter for the extended Debye-Hückel equation, equation (1.49)</td>
</tr>
<tr>
<td>( c )</td>
<td>Molar concentration (mol·L(^{-1}))</td>
</tr>
<tr>
<td>( c_d )</td>
<td>Adjustable parameter for the density model, equation (1.19)</td>
</tr>
<tr>
<td>( c_\nu )</td>
<td>Speed of light (m·s(^{-1}))</td>
</tr>
<tr>
<td>( c_L )</td>
<td>Parameter, equation (3.13)</td>
</tr>
<tr>
<td>( c_{eq} )</td>
<td>Concentration corrected for the hydrolysis of CH(_3)COO(^-) and amphiprotic ionization of H(_2)PO(_4)(^-)</td>
</tr>
<tr>
<td>( c_i ) (i = 1-7)</td>
<td>Coordination coefficients to describe the number of solvent molecules hydrogen bonded to solutes, equations (6.12) and (6.13)</td>
</tr>
<tr>
<td>( D^\circ )</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>( d )</td>
<td>Distance between electrodes</td>
</tr>
<tr>
<td>( d_d )</td>
<td>Adjustable parameter for the density model, equation (1.19)</td>
</tr>
<tr>
<td>( E )</td>
<td>Potential of cell</td>
</tr>
<tr>
<td>( E_{ij} )</td>
<td>Junction potential</td>
</tr>
<tr>
<td>( E_{MXOY}^\circ )</td>
<td>Standard potential of a metal-metal oxide reference electrode, M(_X)O(_Y)</td>
</tr>
<tr>
<td>( E_\nu )</td>
<td>Energy at level ( \nu )</td>
</tr>
<tr>
<td>( E^\circ )</td>
<td>Potential of reference cell</td>
</tr>
<tr>
<td>( e )</td>
<td>Charge on an electron (C)</td>
</tr>
<tr>
<td>( e_d )</td>
<td>Adjustable parameter for the density model, equation (1.19)</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday’s constant (C·mol(^{-1}))</td>
</tr>
<tr>
<td>( F_{vis}^i )</td>
<td>Force due to dielectric friction, equation (1.86)</td>
</tr>
</tbody>
</table>
$F_i$  Force due to stress acting on the local field of an ion’s surface, equation (1.86)

$F_i^*$  Force due to electrostatic interactions between the surrounding ions with each other and ion, i, equation (1.86)

$f$  Frequency (s$^{-1}$)

$f_d$  Adjustable parameter for the density model, equation (1.19)

$f_B$  Friction coefficient

$f_{H2}$  Fugacity of H$_2$(g)

$f_E$  Force applied by external field, equation (1.96)

$g$  Parameter for the Born equation, equation (1.18)

$g_d$  Adjustable parameter for the density model, equation (1.19)

$H_o$  Hammett acidity function

$h$  Planck’s constant (kg·s$^{-1}$)

$I$  Ionic strength of a solution (mol·L$^{-1}$)

$I_c$  Applied current (A)

$I'$  Integrated intensity of vibration modes measured by Raman spectroscopy

$J_1$  Constant for the FHFP equation, equation (1.71)

$J_2$  Constant for the FHFP equation, equation (1.71)

$j$  Complex number

$K_a$  Ionization constant of an acid

$K_{aq}$  Ionization constant represented in terms of the aquamolality standard state

$K_{1a}$  First ionization constant of a polyprotic acid

$K_{2a}$  Second ionization constant of a polyprotic acid
\( K_b \)  Ionization constant of a base
\( K_c \)  Ionization constant represented in terms of the 1 molar standard state
\( K_{\text{DAc}} \)  Ionization constant of acetic acid in D\(_2\)O
\( K_{\text{D3PO4}} \)  Ionization constant of phosphoric acid in D\(_2\)O
\( K_{\text{HAc}} \)  Ionization constant of acetic acid in H\(_2\)O
\( K_{\text{H3PO4}} \)  Ionization constant of phosphoric acid in H\(_2\)O
\( K_{\text{Kr}} \)  Krichevskii parameter, equation (1.28)
\( K_{\text{sp}} \)  Equilibrium constant for solubility
\( K_{w,\text{D}2\text{O}} \)  Ionization constant of D\(_2\)O
\( K_{w,\text{H}2\text{O}} \)  Ionization constant of H\(_2\)O
\( k \)  Reciprocal radius of the ionic atmosphere
\( k_B \)  Boltzmann’s constant (m·kg·s\(^{-2}\)·K\(^{-1}\))
\( k_{\text{cell}} \)  Cell constant (cm\(^{-1}\))
\( k_{\text{cell,highT}} \)  Cell constant at high temperature (cm\(^{-1}\))
\( k_a \)  Spring constant
\( k_z \)  Constant for short-range hydration effects, equation (1.18)
\( L_{\text{diam}} \)  Length of diamond spacer (mm)
\( L_{\text{Pt}} \)  Total length of inner platinum electrode (mm)
\( L_{\text{saph}} \)  Length of sapphire disk (mm)
\( L_1 \)  Length of inner electrode (mm)
\( L_{1,\text{highT}} \)  Length of inner electrode at high temperature (mm)
\( l_T \)  Distance a proton is transported
\( M \)  Molar mass (g·mol\(^{-1}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_D$</td>
<td>Molar mass of deuterium (g·mol⁻¹)</td>
</tr>
<tr>
<td>$M_{D_2O}$</td>
<td>Molar mass of D₂O (g·mol⁻¹)</td>
</tr>
<tr>
<td>$M_H$</td>
<td>Molar mass of hydrogen (g·mol⁻¹)</td>
</tr>
<tr>
<td>$M_{H_2O}$</td>
<td>Molar mass of H₂O (g·mol⁻¹)</td>
</tr>
<tr>
<td>$M_2$</td>
<td>Molar mass of a solute (g·mol⁻¹)</td>
</tr>
<tr>
<td>$m$</td>
<td>Molality (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_{aq}$</td>
<td>Aquamolality $(\text{(mol solute)} \cdot (55.509 \text{ mol solvent})^{-1})$</td>
</tr>
<tr>
<td>$m_{aq,eq}$</td>
<td>Aquamolality corrected for the hydrolysis of CH₃COO⁻ and amphiprotic ionization of H₂PO₄⁻</td>
</tr>
<tr>
<td>$m_{D^+}$</td>
<td>Molality of D⁺ in solution (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_{H^+}$</td>
<td>Molality of H⁺ in solution (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_{H^+,reference}$</td>
<td>Molality of H⁺ in reference cell (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_{H^+,test}$</td>
<td>Molality of H⁺ in test cell (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_i$</td>
<td>Molality of an ion, i (mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_{stock}$</td>
<td>Molality of stock solution(mol·kg⁻¹)</td>
</tr>
<tr>
<td>$m_W$</td>
<td>Slope of Warburg line</td>
</tr>
<tr>
<td>$m(\text{Fe, sat})$</td>
<td>Molality of Fe(mol·kg⁻¹)</td>
</tr>
<tr>
<td>$N$</td>
<td>Avagadro’s constant (mol⁻¹)</td>
</tr>
<tr>
<td>$P$</td>
<td>Force on hydrogen-bonded water</td>
</tr>
<tr>
<td>$pD$</td>
<td>pH of a deuterated species</td>
</tr>
<tr>
<td>$pH_{298}$</td>
<td>Flow-cell inlet pH at 298 K</td>
</tr>
<tr>
<td>$p_c$</td>
<td>Critical pressure (MPa)</td>
</tr>
<tr>
<td>$p_{c,D_2O}$</td>
<td>Critical pressure of D₂O (MPa)</td>
</tr>
</tbody>
</table>
\( p_{c,H_2O} \)  
Critical pressure of \( H_2O \) (MPa)

\( p_{\text{sat}} \)  
Saturation vapor pressure (MPa)

\( pK_{BH^+} \)  
Indicator acidity value

\( pK_{a,H_2O} \)  
Ionization constant of a species in \( H_2O \) using the molality standard state

\( pK_{aq,D_2O} \)  
Ionization constant of species in \( D_2O \) using aquamolality standard state

\( pK_{aq,H_2O} \)  
Ionization constant of species in \( H_2O \) using aquamolality standard state

\( pK_{aq,OH} \)  
Hydrolysis ionization constant using aquamolality standard state

\( pK_w \)  
Ionization constant of water

\( pK_{w,D_2O} \)  
Ionization constant of \( D_2O \)

\( pK_{w,H_2O} \)  
Ionization constant of \( H_2O \)

\( Q \)  
Equilibrium quotient

\( Q_a \)  
Equilibrium quotient for an acid

\( Q_{sp} \)  
Equilibrium quotient for solubility

\( q \)  
Adjustable parameter for the Meissner equation for NaCl, equation (1.37)

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

\( R_e \)  
Resistance (Ω)

\( R_{ct} \)  
Charge transfer resistance (Ω)

\( R_{e,j} \)  
Electrostatic radius of an ion, j (Å)

\( R_i \)  
Crystallographic radius of an ion, i (Å)

\( R_{x,j} \)  
Crystallographic radius of an ion, j (Å)

\( R_{\text{stokes}} \)  
Effective stokes radius of an ion in solution (Å)

\( R_s \)  
Solution resistance (Ω)

\( R_{\text{Walden}}^{D,H} \)  
Walden product ratio

xxxv
\( r_1 \) Radius of inner electrode (mm)

\( r_2 \) Radius of outer electrode (mm)

\( S \) Onsager limiting slope

\( T_{b,D_2O} \) Normal boiling point of \( D_2O \) (K)

\( T_{b,H_2O} \) Normal boiling point of \( H_2O \) (K)

\( T_c \) Critical temperature (K)

\( T_{c,D_2O} \) Critical temperature of \( D_2O \) (K)

\( T_{c,H_2O} \) Critical temperature of \( H_2O \) (K)

\( T_{m,D_2O} \) Normal melting point of \( D_2O \) (K)

\( T_{m,H_2O} \) Normal melting point of \( H_2O \) (K)

\( t_i^o \) Limiting transference number of an ion, \( i \)

\( t_+^o \) Limiting transference number of a cation

\( t_-^o \) Limiting transference number of an anion

\( V \) Voltage (V)

\( V_m \) Molar volume (cm\(^3\)·mol\(^{-1}\))

\( V_{m,D_2O} \) Molar volume of \( D_2O \) (cm\(^3\)·mol\(^{-1}\))

\( V_{m,H_2O} \) Molar volume of \( H_2O \) (cm\(^3\)·mol\(^{-1}\))

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

\( V_{A^-}^o \) Partial molar volume of species \( A^- \) (cm\(^3\)·mol\(^{-1}\))

\( V_{HA}^o \) Partial molar volume of a weak acid (cm\(^3\)·mol\(^{-1}\))

\( v_i^{el} \) Velocity of an ion, \( i \)

\( v_i^o \) Velocity of an ion, \( i \), at infinite dilution

\( W \) Warburg impedance
\( w_a \)  Mass of particle, a (g)
\( w_b \)  Mass of particle, b (g)
\( w_{\text{salt,stock}} \)  Mass of salt used to make the stock solution (g)
\( w_{\text{solvent,stock}} \)  Mass of solvent used to make the stock solution (g)
\( w_{\text{solvent,dilute}} \)  Mass of solvent used to dilute stock solution (g)
\( w_{\text{stock,dilute}} \)  Mass of stock solution used in dilution (g)
\( w_1 \)  Mass of solvent (g)
\( w_2 \)  Mass of a solute (g)
\( X \)  Electric field
\( X_c \)  Reactive capacitance
\( Z \)  Impedance
\( Z_{\text{Im}} \)  Imaginary impedance component
\( Z_{\text{Re}} \)  Real impedance component
\( z \)  Absolute value of charge
\( z_j \)  Absolute value of charge on ion j
\( \partial \)  Partial derivative

*Greek Symbols and Variables*

\( \alpha \)  Degree of ionization
\( \alpha_W \)  Component of Warburg impedance
\( \alpha_2 \)  Degree of hydrolysis
\( \beta \)  Compressibility of the solvent (Pa\(^{-1}\))
\( \beta_2 \)  Second degree of dissociation
\( \gamma_i \) Activity coefficient of an ion, \( i \)

\( \gamma_{H^+, \text{reference}} \) Activity coefficient of \( H^+ \) in reference cell

\( \gamma_{H^+, \text{test}} \) Activity coefficient of \( H^+ \) in test cell

\( \gamma^\circ \) Mean ionic activity coefficient

\( \Delta \) Difference

\( \Delta C_p^\circ \) Change in the partial molar heat capacity (J·K\(^{-1}\)·mol\(^{-1}\))

\( \Delta G_r^\circ \) Gibbs free energy of reaction (kJ·mol\(^{-1}\))

\( \Delta \text{solv} G^\circ \) Gibbs free energy of solvation (kJ·mol\(^{-1}\))

\( \Delta \text{solv} G_j^\circ \) Gibbs free energy of solvation of ion, \( j \) (kJ·mol\(^{-1}\))

\( \Delta H^\circ \) Change in standard enthalpy (kJ·mol\(^{-1}\))

\( \Delta S^\circ \) Change in standard entropy (J·K\(^{-1}\)·mol\(^{-1}\))

\( \Delta V^\circ \) Change in partial molar volume (cm\(^3\)·mol\(^{-1}\))

\( \Delta a_d \) Adjustable parameter for the density model, equation (3.15)

\( \Delta b_d \) Adjustable parameter for the density model, equation (3.15)

\( \Delta c_d \) Adjustable parameter for the density model, equation (3.15)

\( \Delta e_d \) Adjustable parameter for the density model, equation (3.15)

\( \Delta p \text{K}_a \) \( p \text{K}_{a, D_2O} - p \text{K}_{a, H_2O} \)

\( \Delta p \text{K}_\text{aq} \) \( p \text{K}_{\text{aq}, D_2O} - p \text{K}_{\text{aq}, H_2O} \)

\( \Delta \nu \) Loss of a vibration frequency, equation (1.97)

\( \delta c \) Absolute uncertainty in concentration

\( \delta m \) Absolute uncertainty in molality

\( \delta R_s \) Absolute uncertainty in \( R_s \)

\( \delta_{\text{standardization}} \) Absolute standard deviation associated with standardization
\( \delta \Lambda^o \)  Absolute uncertainty in \( \Lambda^o \)
\( \delta \kappa_{\text{corr}} \)  Absolute uncertainty in cell corrected specific conductivity
\( \varepsilon \)  Dielectric constant of a medium
\( \varepsilon_{D_2O} \)  Dielectric constant of \( D_2O \)
\( \varepsilon_{H_2O} \)  Dielectric constant of \( H_2O \)
\( \varepsilon_w \)  Dielectric constant of a solvent
\( \eta \)  Viscosity of a medium (P)
\( \eta_{D_2O} \)  Viscosity of \( D_2O \) (P)
\( \eta_{H_2O} \)  Viscosity of \( H_2O \) (P)
\( \eta_w \)  Viscosity of a solvent (P)
\( \kappa \)  Specific conductivity of a solution (S·cm\(^{-1}\))
\( \kappa_{\text{corr}} \)  Cell corrected specific conductivity (S·cm\(^{-1}\))
\( \kappa_{\text{exp}} \)  Experimental value of specific conductivity (S·cm\(^{-1}\))
\( \kappa_{\text{eq}} \)  Corrected specific conductivity (S·cm\(^{-1}\))
\( \kappa_{w}^{\text{exp}} \)  Experimental specific conductivity of water (S·cm\(^{-1}\))
\( \kappa_{w} \)  Specific conductivity of pure water (S·cm\(^{-1}\))
\( \Lambda \)  Molar conductivity (S·cm\(^2\)·mol\(^{-1}\))
\( \Lambda^{\exp} \)  Experimental molar conductivity (S·cm\(^2\)·mol\(^{-1}\))
\( \Lambda^{\exp,eq} \)  Corrected experimental molar conductivity (S·cm\(^2\)·mol\(^{-1}\))
\( \Lambda^o \)  Molar conductivity at infinite dilution (or limiting molar conductivity)
\( \Lambda^{\text{calc}}^o \)  Calculated value of \( \Lambda^o \) (S·cm\(^2\)·mol\(^{-1}\))
\( \Lambda^{\text{trial}}^o \)  Trial value of \( \Lambda^o \) (S·cm\(^2\)·mol\(^{-1}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda )</td>
<td>Ionic molar conductivity (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_{A^-}^\circ )</td>
<td>Limiting molar conductivity of the acetate anion (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_E^\circ )</td>
<td>Excess limiting molar conductivity of an ion (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_{E,D}^\circ )</td>
<td>Excess limiting molar conductivity of an ion in D(_2)O (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_{E,H}^\circ )</td>
<td>Excess limiting molar conductivity of an ion in H(_2)O (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_{H^+}^\circ )</td>
<td>Limiting molar conductivity of H(^+) (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_i^\circ )</td>
<td>Limiting molar conductivity of an ion, i (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_+^\circ )</td>
<td>Limiting molar conductivity of a cation (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_-^\circ )</td>
<td>Limiting molar conductivity of an anion (S·cm(^2)·mol(^{-1}))</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Reduced mass (g)</td>
</tr>
<tr>
<td>( \nu_{H,1} )</td>
<td>O-H stretching frequency, equation (1.99)</td>
</tr>
<tr>
<td>( \nu_{H,2} )</td>
<td>O-H stretching frequency, equation (1.99)</td>
</tr>
<tr>
<td>( \nu_{H,3} )</td>
<td>O-H stretching frequency, equation (1.99)</td>
</tr>
<tr>
<td>( \nu_{H,4} )</td>
<td>O-H stretching frequency, equation (1.100)</td>
</tr>
<tr>
<td>( \nu_{H,5} )</td>
<td>O-H stretching frequency, equation (1.100)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density of a solution (g·cm(^{-3}))</td>
</tr>
<tr>
<td>( \rho_{D2O} )</td>
<td>Density of D(_2)O (g·cm(^{-3}))</td>
</tr>
<tr>
<td>( \rho_{H2O} )</td>
<td>Density of H(_2)O (g·cm(^{-3}))</td>
</tr>
<tr>
<td>( \rho_w )</td>
<td>Density of the solvent (g·cm(^{-3}))</td>
</tr>
<tr>
<td>( \rho_{w,r} )</td>
<td>Reduced density of the solvent</td>
</tr>
<tr>
<td>( \rho^* )</td>
<td>Critical density of the solvent (g·cm(^{-3}))</td>
</tr>
<tr>
<td>( \sigma^u )</td>
<td>Raman scattering cross section of a species (cm(^2))</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\tau_{D,D_2O}$</td>
<td>Dielectric relaxation time for D$_2$O (s)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Phase angle</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Mol fraction of solute</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$\omega_M$</td>
<td>Angular frequency of a harmonic oscillator ($s^{-1}$)</td>
</tr>
</tbody>
</table>
PART I:

INTRODUCTION AND EXPERIMENTAL METHODS
CHAPTER 1
INTRODUCTION

1.1 Overview

High-temperature high-pressure aqueous solution chemistry, “hydrothermal chemistry”, is a topic of considerable practical interest due to the important role that water plays in geochemistry and industrial technology. In addition, the physical properties of water under hydrothermal conditions are very different than those at near-ambient conditions, and the effect that this plays on the behavior of species in aqueous solutions is scientifically fascinating. In the early 1900’s, Noyes et al. (1904, 1907, 1908) reported conductance measurements on water, salts, acids and bases at temperatures as high as 573 K, which they used to calculate equilibrium constants. Few additional studies under hydrothermal conditions were made until the 1950’s, when there became an interest in corrosion processes in steam generating plants and nuclear reactors (Mesmer et al., 1997; Weingärtner and Franck, 2005). In the 1970’s, interest in geochemical processes in hydrothermal vents provided further drive (Henley and Ellis, 1983).

The measurement of the thermophysical properties of water under hydrothermal conditions began more than 100 years ago, when steam became a fluid used in mechanical and electrical power generation. Early in the 1900’s, thermodynamic tables and charts were developed, and equations for the properties of water have been around since 1934 (Smith and Keyes, 1934; Saul and Wagner, 1987; Sato et al., 1991). The thermophysical properties of aqueous species have also been measured since Noyes et al.
work in the early 1900’s. In addition to conductivity, methods for measuring ionization constants under hydrothermal conditions include solubility, EMF, Raman, UV-VIS spectroscopy and flow-calorimetry (Marshall, 1985; Tremaine et al., 2004). Predictive algorithms for properties of aqueous species at temperatures up to 623 K have also been around since 1964 (Criss and Cobble, 1964; Shock and Helgeson, 1988; Sverjenksy et al., 1997).

The hydrothermal properties of solutes in an isotopically heavier analog of water, heavy water or deuterium oxide (\(2^1\)\(^2\)H\(_2\)O or D\(_2\)O), are also of significant interest. The use of D\(_2\)O by the Canadian nuclear industry in the CANadium Deuterium Uranium (CANDU) nuclear reactor provides a strong industrial drive for understanding the nature of this solvent at elevated temperatures and pressures. The increase in the molar mass of D\(_2\)O (\(M_{D2O} = 20.0276 \, \text{g} \cdot \text{mol}^{-1}\)), compared to H\(_2\)O (\(M_{H2O} = 18.0153 \, \text{g} \cdot \text{mol}^{-1}\)), causes small, but detectable differences in the properties of the solvent, commonly referred to as a deuterium solvent isotope effect (Laughton and Robertson, 1969; Arnett and McKelvey, 1969). At 298 K, both H\(_2\)O and D\(_2\)O have high polarity and strong hydrogen bonds, which results in high dielectric constants, \(\varepsilon_{H2O} = 78.50\) and \(\varepsilon_{D2O} = 78.25\) (Fernández et al., 1995; Okada et al., 1999). As temperature increases, the average number and strength of the hydrogen bonds in both H\(_2\)O and D\(_2\)O weaken, which results in a decrease in the densities and the dielectric constants of both solvents (Tödhidee, 1972; Dass, 1986; Okada et al., 1999; Foustoukos and Mysen, 2012).

The differences in the thermophysical properties of species in D\(_2\)O vs. H\(_2\)O can be separated into primary and secondary deuterium isotope effects. Primary isotope effects are caused by the replacement of hydrogen by deuterium on a particular species, and
secondary effects are due to the differences in ion solvation upon changing the solvent from H₂O to D₂O (Halpern, 1935; Arnett and McKelvey, 1969; Friedman and Krishnan, 1973).

Measurements of deuterium isotope effects on ionization and chemical equilibria at 298 K were extensive up until the 1960’s, covering a wide array of organic and inorganic species (Laughton and Robertson, 1969; Arnett and McKelvey, 1969). Since the 1960’s, measurements at near-ambient conditions have focused more often on deuterium isotope effects on the kinetics of chemical reactions; as well as the role of these effects in various biological processes; such as enzyme binding interactions (Wade, 1999; Wolfsberg et al., 2010). In addition, several authors have measured differences in the partial and apparent molar volumes of strong electrolytes in D₂O vs. H₂O, at temperatures below 373 K (Dessauges et al., 1980; Allred and Woolley, 1981; Jákli, 2007).

Measurements of deuterium isotope effects on ionization and chemical equilibria have also been made under hydrothermal conditions, but these are few. The ionization constants of D₂O and D₂PO₄⁻ were determined using EMF methods, at temperatures up to 573 K, by Shoesmith and Lee (1976) and Mesmer and Herting (1978). Ionization constants of DSO₄⁻ were calculated from solubility measurements of Ag₂SO₄ in solutions of D₂SO₄, up to 498 K, by Lietzke and Stoughton (1963).

Recently, our group began to measure deuterium isotope effects on the properties of simple acids and bases at elevated temperatures and pressures. The purpose of these measurements is to provide information to optimize D₂O coolant chemistry in the CANDU reactor and to probe the nature of solute-solvent effects as a function of
temperature and pressure. Measurements of the ionization constants of a colorimetric indicator (β-naphthol) and the boric acid/borate buffer system were made using UV-visible spectroscopy, from 498 to 573 K (Bulemela and Tremaine, 2009). Apparent and partial molar volumes of NaCl, HCl/DCl and NaOH/NaOD were measured using high-temperature high-pressure densitometry, at 523 and 573 K (Trevani et al., 2007).

The purpose of this thesis project is to investigate the nature of deuterium isotope effects on the ionization constants of weak acids and the transport properties of ions in aqueous solution under hydrothermal conditions. I hope to provide information that can lead to a fundamental understanding of deuterium isotope effects, as a function of temperature and pressure, which can eventually be used to create a model to predict deuterium isotope effects. In collaboration with my co-worker, Dr. Hugues Arcis, I set out to measure the ionization constants for two model systems (acetic acid, CH$_3$COOH, and phosphoric acid, H$_3$PO$_4$) in H$_2$O and D$_2$O up to 573 K using alternating current (AC) conductance. I have also used these conductance measurements to quantify the differences in the transport of ions in D$_2$O vs. H$_2$O.

1.2 Rationale

1.2.1 Introduction to the CANDU Nuclear Reactor

The CANDU nuclear reactor is a unique design, when compared to other nuclear reactors around the world, in that it uses D$_2$O rather than H$_2$O as a coolant and heat transport medium (McFarland et al., 2001; AECL, 2012). D$_2$O has a low cross section for neutron absorption, and its use as the primary coolant and moderator fluid permits the use of un-enriched natural uranium as the reactor fuel (McFarland et al., 2001; Steed,
As shown below in Figure 1.1, the CANDU reactor uses two coolant circuits. The primary coolant circuit contains D$_2$O and consists of: (i) zirconium pressure tubes, (ii) carbon steel inlet and outlet feeder tubes and (iii) an inconel (nickel-chromium alloy) steam generator. The secondary coolant circuit contains H$_2$O and consists of an inconel steam generator, turbine and condenser tubes (cooled by external water source such as a lake or ocean). Heat exchange from the primary circuit through the inconel boiler tubes generates the steam that drives the turbine in the secondary circuit. After, the steam is condensed using H$_2$O from the external water source, and then pumped back to the boiler. The zirconium pressure tubes in the primary coolant circuit contain zirconium-clad natural uranium fuel bundles. Fission of the uranium releases heat, increasing the temperature of the D$_2$O coolant from 523 to 573 K, as it passes through the pressure tubes. The hot D$_2$O travels through the outlet feeder tubes to the inconel steam generator. The D$_2$O in the primary coolant circuit is cooled back to 523 K as it is pumped through the steam generator. The cooled D$_2$O is then pumped through the inlet feeder tubes and back to the pressure tubes to repeat the cycle.

1.2.2 The Hydrolysis and Solubility of Magnetite

The inlet and outlet feeder tubes of the primary circuit are constructed of carbon steel. A passivating layer of magnetite (Fe$_3$O$_4$) on the inner surface of these tubes prevents corrosion of the steel (Rocchini, 1994; Chung, 2010). Slow dissolution of the magnetite layer over time causes the walls of the feeder tubes to thin, which reduces the safety margin used to maintain the pressure conditions within the primary circuit, thus reducing their operating lifetime (Chung, 2010).
Figure 1.1  Schematic of the CANDU reactor, as reported by McFarland et al. (2001) and Steed (2007). 1, CANDU reactor housing unit; 2, Zr-clad un-enriched UO$_2$ fuel bundles; 3, Moderator; 4, Pressure tubes (Zr); 5, Feeder tubes (carbon steel with Fe$_3$O$_4$ inner passivation layer); 6, Steam generator (inconel); 7, Steam generator (inconel); 8, Turbine; 9, Converter; 10, Condenser tubes (H$_2$O coolant comes from outside source). This figure has been adapted from Gonyeau (2009).
Dissolution of the magnetite layer depends upon the chemical and hydrodynamic conditions within the primary cooling circuit. Studies of Fe$_3$O$_4$ solubility in H$_2$O under hydrothermal conditions have been conducted by Sweeton and Baes (1970), Tremaine and LeBlanc (1980) and Ziemniak et al. (1995), who have shown that the temperature dependence of the solubility gradient of Fe$_3$O$_4$ is pH dependent. Measurements reported by Tremaine and LeBlanc (1980) are shown in Figure 1.2 below. The data indicate that when the pH, measured at 298 K (pH$_{298}$), is equal to 9.3, there is a negative solubility gradient as temperature increases from 523 to 573 K. This negative solubility gradient would cause Fe$_3$O$_4$ to precipitate in the reactor core. $^{59}$Co, a low-level impurity found within piping and valves, is released during corrosion as a dissolved species, in suspension as a component of oxide particulates, and as a solid solution in magnetite (Basque, 1993). $^{59}$Co can undergo neutron capture as it passes through the reactor core and transforms into $^{60}$Co, a dangerous radionuclide. Precipitation of Fe$_3$O$_4$ in the reactor core increases the residence time of $^{59}$Co, and its exposure to neutrons, resulting in high $^{60}$Co radiation fields. At pH$_{298}$ 10.3, magnetite has a positive solubility gradient at temperatures from 523 to 573 K (Tremaine and LeBlanc, 1980). Although operating at this pH minimizes any Fe$_3$O$_4$ precipitation within the reactor core, it also causes the feeder tubes to thin at an accelerated rate. At pH$_{298}$ 9.8, the solubility gradient is not as positive as that at pH$_{298}$ 10.3.

Accurate measurements of the solubility of Fe$_3$O$_4$ in H$_2$O at elevated temperatures and pressures are challenging, due to the redox chemistry of the dissolution reactions, the very low solubility of Fe$_3$O$_4$ in water and the experimental challenges of determining the
Figure 1.2 Temperature dependence of Fe$_3$O$_4$ solubility, as reported by Tremaine and LeBlanc (1980). Experimental data points at pH$_{298} = 9.3$ (□), experimental data points at pH$_{298} = 9.8$ (Δ) and experimental data points at pH$_{298} = 10.3$ (○). The solid lines (—) correspond to the least-square parameters fitted by Tremaine and Leblanc (1980) to their overall data set.
equilibrium pH. Magnetite dissolves to form iron(II) hydrolyzed species according to the following reaction:

\[
\frac{1}{3} \text{Fe}_3\text{O}_4 + (2-b)H^+ + \frac{1}{3}H_2 \rightleftharpoons \text{Fe(OH)}_{b^{2-b}} + \frac{4}{3}(4-b)\text{H}_2\text{O} \tag{1.1}
\]

At high pH, the solubility equilibria also include iron(III) species (Tremaine and LeBlanc, 1980):

\[
\frac{1}{3} \text{Fe}_3\text{O}_4 + (3-b)H^+ \rightleftharpoons \text{Fe(OH)}_{b^{3-b}} + \frac{1}{6}H_2 + \frac{4}{3}(4-b)\text{H}_2\text{O} \tag{1.2}
\]

The solubility of the hydrolyzed species in equation (1.1) is pH dependent, according to the equations for the equilibrium quotient, \(Q\):

\[
Q = \frac{m(\text{Fe(OH)}_{b^{2-b}})}{p(H_2)^{1/3} \cdot m(H^+)^{2-b}} \tag{1.3}
\]

\[
\log[m(\text{Fe(OH)}_{b^{2-b}})] = \log(Q) - (2-b) \cdot \log[m(H^+)] - (1/3) \cdot \log[p(H_2)] \tag{1.4}
\]

Similar expressions for Fe\(^{3+}\) species can be derived from equation (1.2):

\[
Q = \frac{m(\text{Fe(OH)}_{b^{3-b}}) \cdot p(H_2)^{1/6}}{m(H^+)^{3-b}} \tag{1.5}
\]

\[
\log[m(\text{Fe(OH)}_{b^{3-b}})] = \log(Q) - (3-b) \cdot \log[m(H^+)] + (1/6) \cdot \log[p(H_2)] \tag{1.6}
\]

The contribution of different hydrolyzed species is plotted as a function of equilibrium pH in Figure 1.3 below. Experimental challenges arise because: (i) the solubility of \(\text{Fe}_3\text{O}_4\) is very low (as shown by the small values of \(m(\text{Fe, sat})\) in Figure 1.2), (ii) equilibrium between magnetite, hydrolyzed species and hydrogen must be demonstrated
Figure 1.3  The molality of various Fe(OH)$_2$$^{2-}$ and Fe(OH)$_3$$^{3-}$ aqueous species as a function of pH$_{298}$: Fe$^{2+}$ (●), FeOH$^+$ (△), Fe(OH)$_2$ (■), Fe(OH)$_3$ (▲), Fe(OH)$_4$$^{2-}$ (○), Fe(OH)$_3$ (□) and Fe(OH)$_4$$^-$(▽). The solid lines are the corresponding slopes of equation (1.4) and (1.6), present for visualization purposes only. The thick solid line shows the total molality of all Fe species at each pH.
and (iii) during a solubility measurement, there is a risk of precipitating soluble iron, especially upon cooling the water samples for analysis (Sweeton and Baes, 1970; Tremaine et al., 1977; Tremaine and LeBlanc, 1980; Ziemniak et al., 1995). The equilibrium pH must also be accurately known. These chemical and experimental challenges have made past measurements of Fe$_3$O$_4$ solubility under hydrothermal conditions in H$_2$O difficult. The most accurate solubility data (like those seen in Figure 1.2) contain statistical and systematic uncertainties of up to one order of magnitude.

To quantify high-temperature high-pressure Fe$_3$O$_4$ solubility in D$_2$O, measurements under such conditions would have to be made and then compared directly to measurements in H$_2$O (Sweeton and Baes, 1970; Tremaine et al., 1977; Tremaine and LeBlanc, 1980; Ziemniak et al., 1995). Direct comparisons, however, will probably not provide any statistically significant differences in Fe$_3$O$_4$ solubility in D$_2$O vs. H$_2$O, due to the uncertainties mentioned above.

1.2.3 Basic Research on Solvation at High Temperatures and Pressures

Frank and Evans (1945) and Frank and Wen (1957) have used a description of “ice-like” water structures around ions at 298 K to explain hydration and to account for the dielectric and relative viscosity properties of aqueous ions (Hasted et al., 1948; Mason et al., 1952). Raman spectroscopy measurements have also found that the addition of electrolytes to H$_2$O causes a breakdown of hydrogen-bonded water structure, which is attributed to the formation of a primary solvation shell about the electrolyte ion (Walrafen, 1966, 1970). X-ray absorption fine structure, “EXAFS”, measurements by Pfund et al. (1994) and Wallen et al. (1998) have been used to characterize ion-solvent
interactions from near-ambient to supercritical conditions, which have been supported by molecular dynamic simulations (Balbuena et al., 1996; Guàrdia et al., 2006).

Measuring the thermophysical properties of hydrothermal aqueous systems is important in order to probe the nature of ion-solvation and to develop thermodynamic equations of state (Tremaine et al., 2004). Partial molar properties of aqueous species are obtained by extrapolating measured apparent molar properties to infinite dilution, where the only type of interaction that can be attributed to the property is a solute-solvent one (Anderson and Crerar, 1993). Several equations of state describe standard partial molar properties as a function of temperature and pressure (Tremaine et al., 2004; Majer et al., 2004), which will be discussed in more detail below.

Measurements of ion transport under hydrothermal conditions can also provide information that can be used to probe the nature of solute-solvent interactions. Ions in aqueous solution change the local solvent sphere around the ion, causing its viscosity to be either higher or lower than that of the bulk solvent (Frank and Wen 1957; Kay, 1991).

1.3 Physical Properties of H$_2$O and D$_2$O

1.3.1 Properties at Ambient Conditions

Values of density, $\rho_{H2O}$, viscosity, $\eta_{H2O}$, dielectric constant, $\varepsilon_{H2O}$, and ionization constant, $pK_{w,H2O}$, at 298 K are shown in Table 1.1 below, as well as the normal boiling point, $T_{b,H2O}$, and normal melting point, $T_{m,H2O}$ (Sweeton et al., 1974; Kestin et al., 1984; Lide, 1990-1991; Fernández et al., 1995; Wagner and Pruß, 2002). Hydrogen bonding in
Table 1.1. Values of densities, viscosities, dielectric constants and ionization constants for H$_2$O and D$_2$O at 298 K. Values of the normal boiling points and normal melting points of H$_2$O and D$_2$O.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\rho$</th>
<th>$\eta$</th>
<th>$\varepsilon$</th>
<th>$pK_w$</th>
<th>$T_b$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g·cm$^{-3}$</td>
<td>P</td>
<td></td>
<td>K</td>
<td>K</td>
<td>K</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.997047</td>
<td>0.008901</td>
<td>78.50</td>
<td>13.993</td>
<td>373.15</td>
<td>273.15</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>1.104500</td>
<td>0.010950</td>
<td>78.25</td>
<td>14.951</td>
<td>374.57</td>
<td>276.97</td>
</tr>
</tbody>
</table>
H$_2$O has been studied using Raman spectroscopy (Walrafren, 1964), X-ray diffraction (Narten and Levy, 1971), neutron diffraction (Soper and Phillips, 1986) and by dielectric relaxation (Kaatze, 1993). At 298 K, strong hydrogen bonding favors tetrahedral-like orientations, with an average coordination number near 4 (Nakahara, 2004). The strong hydrogen bonding at 298 K also causes H$_2$O to have a high dielectric constant, viscosity and density, and to have a low ionization constant, $K_w$ (Hasted, 1972; Kell, 1972; Sweeton et al., 1974; Uematsu and Franck, 1980; Wagner and Pruß, 2002).

Differences in the properties of D$_2$O vs. H$_2$O at 298 K that arise from differences in O-D vs. O-H bond strength are primarily the result of the difference in the reduced mass of O-D vs. O-H. These can be described by treating O-H as a harmonic oscillator (McQuarrie and Simon, 1997). According to Hooke’s law, the angular frequency of a harmonic oscillator, $\omega_M$, is defined as follows:

$$\omega_M = \frac{k_s}{\sqrt{\mu}},$$  \hspace{1cm} (1.7)

where $k_s$ is a spring constant and $\mu$ is the reduced mass, defined as:

$$\mu = \frac{w_a \cdot w_b}{w_a + w_b},$$ \hspace{1cm} (1.8)

with $w_a$ and $w_b$ being the mass of each particle in a 2-particle system. If H is changed to D, with the oxygen remaining constant, the reduced mass of the 2-particle system increases. The energy levels of a harmonic oscillator are defined by the equation:

$$E_{\nu} = \frac{k_s}{\mu} \left( \nu + \frac{1}{2} \right),$$ \hspace{1cm} (1.9)

with $\nu = 0, 1, 2, 3\ldots$ As a result of its larger reduced mass, $\mu$, the value of the zero-point energy, $E_0$, is lower for O-D than for O-H, resulting in a stronger bond. Quantum
mechanical studies of liquid D\textsubscript{2}O and H\textsubscript{2}O indicate, from radial distribution functions, that D\textsubscript{2}O is in fact more structured than H\textsubscript{2}O at 298.15 K, and that O\cdots D-O bond angles are more linear than O\cdots H-O bonds (Jancso and Van Hook, 1974; Kuharski and Rossky, 1985; Kohen and Limbach, 2010).

The stronger hydrogen bonding in D\textsubscript{2}O also results in different thermodynamic and transport properties at 298.15 K. The molar volume of D\textsubscript{2}O at 298.15 K is smaller than that of H\textsubscript{2}O (Hill, 1982; Wagner and Pruß, 2002). The normal boiling point of D\textsubscript{2}O is higher than that of H\textsubscript{2}O. The viscosity of D\textsubscript{2}O is larger than that of H\textsubscript{2}O. The dielectric constant for D\textsubscript{2}O is slightly smaller than that for H\textsubscript{2}O at 298.15 K (Arnett and McKelvey, 1969).

1.3.2 High-Temperature High-Pressure Properties

The \textit{PVT} properties of high-temperature water and steam have been measured extensively and, starting in the 1930’s, standard formulations were adopted by the International Association for the Properties of Water and Steam (IAPWS) to calculate the thermodynamic and transport properties for water as a function of temperature and pressure (Harvey and Friend, 2004). The current formulation uses the Helmholtz energy to calculate the thermodynamic properties of water as a function of temperature and pressure (Wagner and Pruß, 2002). Kestin and Sengers (1986) have provided a relationship to calculate accurate values of viscosity, $\eta_{\text{H}_2\text{O}}$, as a function of temperature and density. Values of the dielectric constant, $\varepsilon_{\text{H}_2\text{O}}$, have also been measured extensively and these can be calculated as a function of temperature and density from the equations provided by Uematsu and Franck (1980) and Fernández \textit{et al.} (1995). The most recent
formulation by Fernández has been adopted as standard by IAPWS and is available as an ASME/IAPWS NIST database. Marshall and Franck (1981) have also derived an equation to describe how values of \( pK_w \) behave as a function of temperature and density, which has been adopted by IAPWS (ASME and IAPWS Formulation for water and steam, version 10.0).

Values of the saturation vapor pressure for \( \text{H}_2\text{O} \), \( p_{\text{sat}} \), are shown as a function of temperature, from 273.15 K up to the critical point of water (\( T_{c,\text{H}_2\text{O}} = 647.10 \) K, \( p_{c,\text{H}_2\text{O}} = 22.06 \) MPa, Wagner and Pruß, 2002), in Figure 1.4. Other properties of \( \text{H}_2\text{O} \) at \( p_{\text{sat}} \): \( \rho_{\text{H}_2\text{O}} \), \( \eta_{\text{H}_2\text{O}} \), and \( \varepsilon_{\text{H}_2\text{O}} \), are plotted as a function of temperature, in Figures 1.5 to 1.7, respectively.

It is known that as temperature increases, the thermodynamic and transport properties of liquid \( \text{H}_2\text{O} \) begin to change. With increasing temperature, \( \text{H}_2\text{O} \) expands. The thermal motions of individual \( \text{H}_2\text{O} \) molecules also increase with increasing temperature, causing the tetrahedral structures seen at near-ambient conditions to break down. Radial distribution functions presented by Soper (2000) as function of temperature show, through an increased O-H bond distance and a broadening of the O-H neutron scattering peaks, how water expands, becomes more disordered and, by 573.15 K, loses a considerable amount of hydrogen bonding (Harvey and Friend, 2004; Seward and Driesner, 2004). Experiments and molecular dynamic simulations have also shown that as the critical point of the solvent is approached, the coordination number of \( \text{H}_2\text{O} \) decreases (Balbuena et al., 1996; Okada et al., 1999; Seward and Driesner, 2004).
Figure 1.4  Saturation vapor pressure, $p_{\text{sat}}$ (MPa), of H$_2$O as a function of temperature. (⊙) is the critical point of H$_2$O.
Figure 1.5  Density of H$_2$O, $\rho_{\text{H}_2\text{O}}$ (g·cm$^{-3}$), as a function of temperature at $p_{\text{sat}}$ up to the critical point. ($\bigcirc$) is the density of H$_2$O at its critical point.
Figure 1.6  Viscosity of H$_2$O, $\eta_{\text{H}_2\text{O}}$ (P), as a function of temperature at $p_{\text{sat}}$ up to the critical point. (∘) is the viscosity of H$_2$O at its critical point.
Figure 1.7  Dielectric constant of H$_2$O, $\varepsilon_{\text{H}_2\text{O}}$, as a function of temperature at $p_{\text{sat}}$ up to the critical point. (◊) is the dielectric constant of H$_2$O at its critical point.
The density of H₂O (Figure 1.5) is 0.9998 g·cm⁻³ at 273 K. As the temperature increases, the density decreases. With a continued increase in O-H bond distance and greater molecular motion as temperature increases, the density of H₂O continues to decrease, having a value equal to 0.3972 g·cm⁻³ at the critical point. The increase in intermolecular O-H bond distance and greater molecular motion also causes the viscosity of H₂O to decrease as temperature increases (Figure 1.6). The viscosity of H₂O at 273 K is 0.018 P, reducing to a value of 0.0005 P at the critical point. The dielectric constant of H₂O (Figure 1.7) also decreases, from 88 at 273 K to 7 at the critical point. This is due to the decrease in the average number of hydrogen bonds per water molecule with increasing temperature, as well as the increased thermal motion and lower density.

Thermodynamic and transport properties of D₂O under hydrothermal conditions have also been measured. IAPWS has adopted the equations of state for ρD₂O and ηD₂O reported by Hill et al. (1982) and Kestin and Sengers (1986), and NIST has incorporated the IAPWS formulation into a database for pure and binary fluids (REFPROP) in order to calculate these properties as a function of temperature and pressure. There have also been measurements of dielectric relaxation times, τD,D₂O, for D₂O under hydrothermal conditions (Okada et al., 1999). From these measurements, Okada et al. have concluded that values of εD₂O under hydrothermal conditions can be described by the equation of state for εH₂O given by Uematsu and Franck (1980), when H₂O and D₂O are the same at the same temperature and number density.

The density, viscosity, and dielectric constant of D₂O also decrease as temperature increases (Hill et al., 1982; Kestin and Sengers, 1986; Okada et al., 1999), which indicates, when compared to H₂O, that there is a similar expansion of the solvent
and a weakening of hydrogen bonds. Stronger hydrogen bonding in D\textsubscript{2}O vs. H\textsubscript{2}O and the larger molar mass causes the normal boiling point of D\textsubscript{2}O to be greater than that of H\textsubscript{2}O. However, the critical point for D\textsubscript{2}O (\(T_{c,D2O} = 643.89\) K, \(p_{c,D2O} = 21.67\) MPa) is actually lower than the critical point for H\textsubscript{2}O (Kamgar-Parsi et al., 1983).

Several authors have compared differences in the thermophysical properties of D\textsubscript{2}O vs. H\textsubscript{2}O as a function of temperature. Past comparisons of the surface tension of D\textsubscript{2}O vs. H\textsubscript{2}O have shown that the value for D\textsubscript{2}O becomes less, when compared to the value for H\textsubscript{2}O, as temperature is increased (Heiks et al., 1957; Kell, 1972). By comparing experimental relative differences of viscosity for D\textsubscript{2}O vs. H\textsubscript{2}O, Matsunga et al. (1989) have shown that values of \(\eta_{D2O}\) are greater than values of \(\eta_{H2O}\) at near-ambient conditions, but that the ratio of \(\eta_{D2O}/\eta_{H2O}\) approaches unity with increasing temperature. Relative differences in the densities of D\textsubscript{2}O vs. H\textsubscript{2}O show that as temperature increases, the ratio of \(\rho_{D2O}/\rho_{H2O}\) also decreases, approaching unity (Hill, 1982; Wagner and Pruß, 2002). Very recently, Foustoukos and Mysen (2012) have used isotope vapor-liquid fractionation studies to investigate differences in the enthalpy required to rupture hydrogen bonding in D\textsubscript{2}O vs. H\textsubscript{2}O, \(\Delta H_{HB}\), as a function of temperature. They have concluded that higher values of \(\Delta H_{HB}\) for D\textsubscript{2}O vs. H\textsubscript{2}O at lower temperatures represents an increased hydrogen bond strength in D\textsubscript{2}O, when compared to H\textsubscript{2}O, and lower values of \(\Delta H_{HB}\) for D\textsubscript{2}O vs. H\textsubscript{2}O at higher temperatures represents a reduced hydrogen bond strength in D\textsubscript{2}O, when compared to H\textsubscript{2}O.
### 1.4 High Temperature High Pressure Aqueous Chemistry

#### 1.4.1 Ionization Constants and Equations of State

#### 1.4.1.1 Thermodynamics

The temperature dependence of an acid ionization constant, $K_a$, is governed by the Gibbs energy of reaction:

$$\Delta G_r^\circ = -R \cdot T \cdot \ln[K_a],$$  \hspace{1cm} (1.10)

which is defined by the change in standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$) as a function of temperature, $T$ (in K):

$$\Delta G_r^\circ = \Delta H^\circ - T \Delta S^\circ$$  \hspace{1cm} (1.11)

From equations (1.10) and (1.11), we obtain the following relationships that show how the temperature dependence of $K_a$ can be related to standard partial molar properties through Maxwell’s equations (Anderson and Crerar, 1993; Tremaine et al., 2004):

$$\Delta S^\circ = \left( \frac{\partial \Delta G_r^\circ}{\partial T} \right)_p$$  \hspace{1cm} (1.12)

$$\frac{\partial}{\partial T}(R \cdot \ln[K_a]) = \frac{\partial}{\partial T} \left( -\frac{\Delta G_r^\circ}{T} \right) = \frac{\Delta H^\circ}{T^2}$$  \hspace{1cm} (1.13)

Similarly, the pressure dependence upon $K_a$ can also be described by the expression (Anderson and Crerar, 1993):

$$\frac{\partial}{\partial p} (\Delta G_r^\circ) = \Delta V^\circ,$$  \hspace{1cm} (1.14)

where $\Delta V^\circ$ is defined as the change in the partial molar volume of the solution.

Combining equations (1.11) to (1.14) gives the general expression for the change in Gibbs function and ionization constant with respect to temperature and pressure:
\[ dG^\circ_T = \left( \frac{\partial G^\circ_T}{\partial p} \right)_T \cdot dT + \left( \frac{\partial G^\circ_T}{\partial T} \right)_p \cdot dp = \Delta V^\circ \cdot dp + \Delta S^\circ \cdot dT \]  

(1.15)

\[ \ln[K_{a,T}] = \ln[K_{a,298.15}] - \frac{1}{R} \cdot \left[ \frac{1}{T} - \frac{1}{298.15} \right] \cdot \Delta H_{298.15}^\circ + \frac{1}{R} \cdot \int_{298.15}^{T} \frac{\Delta C_p^\circ}{T} \cdot dT \]  

- \frac{1}{R \cdot T} \cdot \int_{298.15}^{T} \Delta C_p^\circ \cdot dT - \frac{1}{R \cdot T} \cdot \int_{1}^{p} \Delta V^\circ \cdot dp \]  

(1.16)

Therefore, according to equations (1.15) and (1.16), the change in standard-state Gibbs function, and \( K_a \), as a function of temperature and pressure is defined by the change in the standard partial molar thermodynamic properties: \( \Delta S^\circ \), \( \Delta V^\circ \), and \( \Delta C_p^\circ \).

Solute-solvent interactions play a key role in the behavior of \( \Delta V^\circ \) and \( \Delta S^\circ \) (through \( \Delta C_p^\circ \)) as temperature and pressure increases (Seward and Driesner, 2004). Therefore, measurements of differences in values of \( \Delta V^\circ \) and \( \Delta C_p^\circ \) in D\(_2\)O vs. H\(_2\)O provide valuable insight into the nature of solute-solvent interactions at elevated temperature and pressure conditions, and can provide an alternate route for investigating deuterium isotope effects. Low-temperature values of \( \Delta V^\circ \) and \( \Delta C_p^\circ \) in D\(_2\)O and H\(_2\)O have been measured by several authors using vibrating-tube densitometers and micro-flow calorimeters (Dessauges et al., 1980; Dutta-Choudhury and Van Hook, 1980; Allred and Woolley, 1981). More recently, our group has also measured values of \( \Delta V^\circ \) for various species in D\(_2\)O under hydrothermal conditions using a high-temperature high-pressure vibrating tube densitometer (Trevani et al., 2007).

1.4.1.2 The Born Equation and Short-Range Hydration Effects

Modeling the partial molar properties of species in aqueous solution at elevated temperatures and pressures has become an important tool to predict the thermodynamics
of ionization reactions under hydrothermal conditions (Majer et al., 2004). The Born equation has been used to describe the change in Gibbs free energy of solvation for an ion, j, when it is taken from the gas phase and placed into a dielectric medium (Born, 1920). This change in the Gibbs free energy of solvation, $\Delta_{\text{solv}} G^\circ_j$, depends upon the dielectric constant of the medium, $\varepsilon$; Avagadro’s constant, $N$; the charge on the ion, $z_j$; and the ion’s “effective” electrostatic radius, $R_{e,j}$ (Shock and Helgeson, 1988; Shock et al., 1992; Sverjensky et al., 1997):

$$\Delta_{\text{solv}} G^\circ_j = \frac{N \cdot e^2 \cdot z_j^2}{2 \cdot R_{e,j}} \left( \frac{1}{\varepsilon} - 1 \right)$$

Equation (1.17) describes the contribution of long-range polarization to ionic solvation, in which H$_2$O is treated solely as a dielectric continuum. Equation (1.17) is therefore useful in modeling the temperature dependence of partial molar properties under hydrothermal conditions, as reported by Criss and Cobble (1964), Helgeson et al. (1981) and Wood et al. (1983). Trevani et al. (2007) have used this technique to model the temperature dependence of $\Delta V^\circ$ for various species in D$_2$O vs. H$_2$O under hydrothermal conditions, and has found that the model fits to their experimental values of $\Delta V^\circ$ for NaCl and NaOH/NaOD fairly well, but less well for HCl/DCl.

Helgeson and co-workers (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992; Sverjensky et al., 1997) have developed a correlation between $R_{e,j}$ and the ion’s crystallographic radius, $R_{x,j}$, to account for the short-range hydration effects in solution:

$$R_{e,j} = R_{x,j} + |Z_j| \cdot (k_z + g)$$

(1.18)
where \( k_z \) is a constant (\( k_z = 0.94 \text{ Å} \) for cations and 0 Å for anions) and \( g \) is dependent upon temperature and pressure.

### 1.4.1.3 The “Density Model”

In order to model the temperature dependence of \( K_a \), several different techniques have been used over the years. Marshall (1970) observed that the logarithm of \( K_a \) had a linear dependence on the density of water. Such a dependence led Marshall and Franck (1981) to develop an expression for the log\( K_w \) of water as a function of temperature, up to 1273 K and 1000 MPa:

\[
\log[K_w] = \left( a_d + \frac{b_d}{T} + \frac{c_d}{T^2} + \frac{d_d}{T^3} \right) + k \cdot \log[\rho_{\text{H}_2\text{O}}] \\
(1.19)
\]

\[
k = \left( e_d + \frac{f_d}{T} + \frac{g_d}{T^2} \right), \\
(1.20)
\]

with \( a_d \) through \( g_d \) being adjustable parameters. From equations (1.19) and (1.20), an equation for the isothermal compressibility of water, \( \beta \), was also derived:

\[
\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{1}{\rho_{\text{H}_2\text{O}}} \left( \frac{\partial \rho_{\text{H}_2\text{O}}}{\partial p} \right)_T \\
(1.21)
\]

In equations (1.19) and (1.20) the adjustable parameters \( a_d \) through \( d_d \) dominate in the lower temperature range, where \( \beta \) is not large and hydrogen-bond “structural” effects dominate. The adjustable parameters \( e_d \) through \( g_d \) are important in the higher temperature range, where \( \beta \) becomes the dominating term. Equations (1.19) and (1.20) have been used as general expressions to model the temperature dependence of log\( K_a \) values for a variety of species as a function of temperature and pressure in \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) (Mesmer et al., 1988; Bulemela and Tremaine, 2009).
1.4.1.4 The HKF Model

At lower temperatures, describing the partial molar properties of aqueous solutions with the Born model is inadequate because of short-range hydrogen bonding effects between the ion and the solvent. Helgeson and co-workers (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Sverjensky et al., 1997) have found that short-range solvation effects ("non-solvation contributions") to the partial molar properties can be represented as a series of adjustable parameters. Addition of these terms to the Born equation has become known as the Helgeson, Kirkham, Flowers (HKF) model. The HKF model expressions for $V^\circ$ and $C_p^\circ$, respectively, are as follows:

$$V^\circ = a_1 + a_2 \cdot \left( \frac{1}{\Psi + p} \right) + \left( a_3 + a_4 \cdot \left( \frac{1}{\Psi + p} \right) \right) \cdot \left( \frac{1}{T - \Theta} \right)$$

$$-\omega \cdot Q + \left( \frac{1}{\varepsilon} - 1 \right) \cdot \left( \frac{\partial \omega}{\partial p} \right)_{T}$$

(1.22)

$$C_p^\circ = c_1 + \frac{c_2}{(T - \Theta)^2} - \left( \frac{2 \cdot T}{(T - \Theta)^3} \right) \cdot \left( a_3 \cdot (p - p_r) + a_4 \cdot \ln \left( \frac{\Psi + p}{\Psi + p_r} \right) \right)$$

$$+ \omega \cdot T \cdot X + 2 \cdot T \cdot Y \cdot \left( \frac{\partial \omega}{\partial T} \right)_{p} - T \cdot \left( \frac{1}{\varepsilon} - 1 \right) \cdot \left( \frac{\partial^2 \omega}{\partial T^2} \right)_{p},$$

(1.23)

where:

$$\omega = \frac{N \cdot e^2 \cdot z^2}{2 \cdot r_{ij}}$$

(1.24)

$$Q = \frac{1}{\varepsilon} \left( \frac{\partial \ln\varepsilon}{\partial p} \right)_{T}$$

(1.25)

$$Y = \frac{1}{\varepsilon} \left( \frac{\partial \ln\varepsilon}{\partial T} \right)_{p}$$

(1.26)
Here, $p_r = 1$ bar, $\Theta = 288$ K, $\Psi = 2600$ bar; and $a_1$ to $a_4$ and $c_1$ to $c_4$ are all adjustable parameters. The HKF model has been used by Helgeson and co-workers (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Sverjensky et al., 1997) to successfully model the temperature dependence of partial molar properties for many ionic and neutral aqueous species to 1273 K. This has been done by fitting the adjustable parameters to experimental values of the partial molar properties for these ionic and neutral aqueous species in the lower-temperature region, and extrapolating them to high temperature with the Born term.

1.4.1.4 The Krichevskii Parameter

As the critical point is approached, densities of the liquid and vapor phases of H$_2$O become indistinguishable, which results in the high compressibility, high heat capacity, low density and low dielectric constant, associated with classic near-critical behavior (Anisimov et al., 2004). The critical locus defines differences in the behavior of the critical properties of the binary mixture relative to those of the pure solvent. As a result of this, the partial molar properties of aqueous solutions of both ionic and neutral species diverge to either positive or negative infinity as the critical point of H$_2$O is approached. The sign of this divergence depends upon the slope of the critical locus. The slope and direction of the critical locus of a solution is defined by the Krichevskii parameter, $K_{Kr}$ (Anisimov et al., 2004). For partial molar volumes, $K_{Kr}$ is defined as follows (Anisimov et al., 2004; Tremaine et al., 2004):
\[
K_{Kr} = \left( \frac{\partial p}{\partial \chi} \right)_{V,T} = \left( \frac{\partial V}{\partial \chi} \right)_{p,T} \cdot \left( -\left( \frac{\partial V}{\partial p} \right)_{T,\chi} \right)^{-1}
\]

(1.28)

Therefore:

\[
V^\circ = \left( \frac{\partial V}{\partial \chi} \right)_{p,T} = K_{Kr} \cdot V \cdot \beta,
\]

(1.29)

where \(\beta\) is the compressibility of the solvent. As the critical point of H\(_2\)O is approached, both \(V^\circ\) and \(\beta\) diverge, but their ratio remains finite. Therefore \(K_{Kr}\) remains finite.

Sedlbauer and Wood (2004) have used the Krichevskii parameter to model the temperature dependences of partial molar properties for species in H\(_2\)O by plotting \(K_{Kr}\) as a function of solvent density. Trevani et al. (2007) have used a similar approach for species in D\(_2\)O vs. H\(_2\)O, plotting \(K_{Kr}\) as a function of reduced solvent density, \(\rho_{w,r}\) (where \(\rho_{w,r} = \rho_w/\rho^*\), with \(\rho^*\) being the critical density of the solvent: \(\rho_{H2O}^* = 0.3220 \text{ g cm}^{-3}\) and \(\rho_{D2O}^* = 0.35799 \text{ g cm}^{-3}\)). By using the reduced density of each solvent (as opposed to just the density), Trevani et al. have represented their values of \(V^\circ\) in D\(_2\)O vs. H\(_2\)O in terms of corresponding states, which has been shown to be effective at representing differences in the properties of solutions in D\(_2\)O vs. H\(_2\)O under hydrothermal conditions.

**1.4.1.5 Activity Coefficient Models**

For an ion, i, in solution, its activity, \(a_i\), is defined as follows:

\[
a_i = m_i \cdot \gamma_i
\]

(1.30)

At infinite dilution, the activity coefficient of the ion solution, \(\gamma_i\), equals one. Therefore, at infinite dilution, \(a_i\) equals the molality of the ion, \(m_i\) (for the hypothetical Henry’s law, \(m^o = 1.0 \text{ mol kg}^{-1}\)) (Anderson and Crerar, 1993).
For aqueous solutions not at infinite dilution, values of the mean ionic activity coefficient, $\gamma_\pm$, have been described by a number of different models, depending upon the ionic strength, $I$, of the solution. Debye and Hückel (1923, 1924) described the behavior of $\gamma_\pm$ for an electrolyte solution, by a primitive model in which long-range coulombic forces within the solution cause the ions in solution to be surrounded by “ionic atmospheres”:

$$\ln[\gamma_\pm] = \frac{-A_{DH} \cdot |z_+ \cdot z_-| \cdot \sqrt{I}}{1 + (B_{DH} \cdot \hat{\alpha}) \cdot \sqrt{I}}$$  \hspace{1cm} (1.31)

Here, $\hat{\alpha}$ is defined as the Debye-Hückel distance of closest approach (in angstroms) and $z$ is the ionic charge. $A_{DH}$ and $B_{DH}$ are the Debye-Hückel parameters (Debye and Hückel, 1923, 1924; Robinson and Stokes, 1965; Fawcett, 2004):

$$A_{DH} = \left( \frac{2 \cdot \pi \cdot N}{1000} \right)^{1/2} \cdot \frac{e^3}{(k_B \cdot \varepsilon_{\text{H}_2\text{O}} \cdot T)^{3/2}} = 4.2021 \cdot 10^6 \cdot \left( \frac{\varepsilon_{\text{H}_2\text{O}} \cdot T}{(k_B \cdot \varepsilon_{\text{H}_2\text{O}} \cdot T)^{3/2}} \right)^{1/2}$$ \hspace{1cm} (1.32)

$$B_{DH} = \left( \frac{8 \cdot \pi \cdot N \cdot e^2}{1000 \cdot k_B} \right)^{1/2} \cdot \frac{1}{(\varepsilon_{\text{H}_2\text{O}} \cdot T)^{1/2}} = 50.29 \cdot 10^8 \cdot \left( \frac{\varepsilon_{\text{H}_2\text{O}} \cdot T}{e_{\text{H}_2\text{O}} \cdot T} \right)^{1/2}$$ \hspace{1cm} (1.33)

where $N$ is Avagadro’s constant, $k_B$ is Boltzmann’s constant and $e$ is the charge on an electron. Equation (1.31) has been found to be sufficient to calculate values of $\gamma_\pm$ for solutions with molalities up to $m = 0.1 \text{ mol} \cdot \text{kg}^{-1}$ (Robinson and Stokes, 1965).

At very low molalities ($m = 1.0 \cdot 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$), $\hat{\alpha}$ in equation (1.31) is no longer needed as an adjustable parameter. Thus, equation (1.31) reduces down to the Debye-Hückel limiting law:

$$\ln[\gamma_\pm] = -A_{DH} \cdot |z_+ \cdot z_-| \cdot \sqrt{I}$$  \hspace{1cm} (1.34)
Pitzer (1991) developed a theoretical model: combining the extended form of the Debye-Hückel limiting law with a virial expansion:

$$\ln[\gamma_{\pm}] = -A_{\text{DH}} \left( \frac{z_e \cdot z_i}{1 + b \cdot \sqrt{T}} + \left( \frac{2}{b} \right) \cdot \ln[1 + b \cdot \sqrt{T}] \right) + 2 \cdot B_{\gamma} \cdot m + 6 \cdot C_{\gamma} \cdot m^2, \quad (1.35)$$

where $b = 1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ and $B_{\gamma}$ and $C_{\gamma}$ are binary and tertiary ion interaction parameters (Pitzer, 1991).

Another approach for calculating values of $\gamma_{\pm}$ is the Lindsay model, which is based on using NaCl(aq) as a model system (Lindsay, 1989, 1990). The Lindsay model assumes that electrolytes of the same symmetry have similar activity coefficients, according to the expression:

$$\log[\gamma_i] = |z_i| \cdot \log[\gamma_{\text{NaCl}}], \quad (1.36)$$

where $z_i$ is the charge on the species. Therefore, the activity coefficients of 1:1 electrolytes can be calculated from the Meissner equation for NaCl:

$$\log[\gamma_{\text{NaCl}}] = -\frac{A_M \cdot \sqrt{T}}{1 + C_M \cdot \sqrt{T}} + \log\left[ 1 + B_M \cdot (1 + 0.1 \cdot I)^q - B_M \right], \quad (1.37)$$

where $A_M$ and $C_M$ are extended Debye-Hückel parameters, and $B_M$ and $q$ are adjustable parameters. Although simple, it is successful to $\sim 1.0 \text{ mol}\cdot\text{kg}^{-1}$ over the temperature range 373 to 573 K. It is known to fail at higher temperatures, when ion association becomes important, and at temperatures below 373 K, where hydrogen bond effects are important.
1.4.2 Transport Properties

1.4.2.1 Ionic Conductivity in Electrolyte Solutions

Theoretical work to explain the movement of ions in solution began with Debye and Hückel (1923, 1924), Onsager (1927, 1936) and MacInnes (1938). They described how the velocity of an ion moving through a solvent would be affected by electrophoretic (solvent movement) and relaxation (re-distribution of charge) effects in the solvent molecules near the ion. In solutions not at infinite dilution, where the ions can influence each other, ion conductivity becomes dependent upon concentration. Kohlrausch (1900) derived a simple empirical expression for the concentration dependence upon the molar conductivity, $\Lambda$, of a solute in aqueous solution:

$$\Lambda = \Lambda^\circ - S \cdot \sqrt{c} ,$$  \hspace{1cm} (1.38)

where $\Lambda^\circ$ is the molar conductivity of the aqueous solution at infinite dilution (limiting molar conductivity) and $S$ is a limiting slope based on the properties of $\text{H}_2\text{O}$. More detailed semi-empirical equations are the Fuoss-Hsai-Fernández-Prini (FHFP) equation and Turk-Blum-Bernard-Kunz (TBBK) equation. These equations (to be discussed in more detail below) consider higher-order contributions to the solution conductivity (such as the radius of the ionic atmosphere and the electrophoretic and relaxation effects).

The limiting molar conductivity for an electrolyte solution, $\Lambda^\circ$, can be defined in terms of individual values of $\lambda^\circ$ for ions $i$ and $j$:

$$\lambda_i^\circ + \lambda_j^\circ = \Lambda^\circ ,$$  \hspace{1cm} (1.39)

Values of the limiting molar conductivity for an ion, $\lambda_i^\circ$, are calculated from limiting transference numbers, $t_i^\circ$:

$$\lambda_i^\circ = t_i^\circ \cdot \Lambda^\circ ,$$  \hspace{1cm} (1.40)
The relationship between the absolute mobility of an ion in a solvent of viscosity, $\eta$, its crystallographic radius, $r$, and its limiting ionic molar conductivity is described by Stokes’ law (Robinson and Stokes, 1965; Kay, 1991):

$$\lambda_i \cdot \eta = \frac{F \cdot e \cdot z}{f_B \cdot \pi \cdot r_i}, \quad (1.41)$$

where $F$ is Faraday’s constant, $\eta$ has units of P and $f_B$ is a friction coefficient, defined as:

$$f_B = \frac{k_B \cdot T}{D^o \cdot \eta \cdot \pi \cdot r_i}, \quad (1.42)$$

where $D^o$ is a diffusion coefficient. Kay (1991) plotted the Walden product, $\lambda_i \cdot \eta_{H2O}$, as a function of $1/r_i$ for a number of cations in aqueous solution at 298 K (shown in Figure 1.8 below) and has shown that there is no linear dependence of $1/r_i$ upon $\lambda_i \cdot \eta_{H2O}$. The larger cations ($\text{Bu}_4\text{N}^+$, $\text{Pr}_4\text{N}^+$, $\text{Et}_4\text{N}^+$ and $\text{Me}_4\text{N}^+$) do show a linear dependence of $\lambda_i \cdot \eta_{H2O}$ with respect to $1/r_i$, indicating that $f_B$ is the same for these species. However, for the smaller cations ($\text{Cs}^+$, $\text{K}^+$ and $\text{Na}^+$), there is no simple linear dependence of $\lambda_i \cdot \eta_{H2O}$ with respect to $1/r_i$, indicating that the friction coefficient changes, depending on the cation.

Other investigations by Nakahara and Ibuki (1986) and Kay (1991) have also proven that the Walden product does not depend upon solvent viscosity. Deviations of the Walden product have been described in terms of various models that introduce the concept of ionic co-spheres, where the co-sphere is a layer of solvent molecules surrounding the ion (several molecules thick) whose properties differ from those of the bulk solvent (Frank and Wen, 1957). Kay (1991) has described these co-spheres as “structure making” (where a higher-localized viscosity of the solvent exists in the co-sphere about the ion, when compared to the bulk solvent), or “structure breaking” (where the localized viscosity of the solvent in the co-sphere is less than the bulk solvent).
Figure 1.8  Walden product, $\lambda_0^0 \eta_{\text{H}_2\text{O}}$, as a function of $1/r_i$ for a number of cations in aqueous solution at 298 K: (●) tetrabutyl ammonium (Bu4N+), (■) tetrapropyl ammonium (Pr4N+), (▲) tetraethyl ammonium (Et4N+), (▲) tetramethyl ammonium (Me4N+), (○) Cs+, (□) K+, (△) Na+. The solid line is a non-linear least squares fit to the data for visualization purposed only.
Jenkins and Marcus (1995) and Marcus (1994, 2009) have reviewed the “structure making” and “structure breaking” properties of ions in terms of viscosity $B$-coefficients, which are used to model how solute-solvent interactions affect the viscosity of a solution as a function of concentration.

Additional work has focused on why values of $\lambda^\circ$ for $H^+$ and $OH^-$ are much larger than other univalent ions in solution. The Grotthuss (“proton hopping”) mechanism is a sequence of proton-transfer processes (Conway et al., 1956; Tada et al., 1992, 1993; Agmon, 1995). As shown in Figure 1.9, “proton hopping” occurs by a rotation of an oxonium ion ($H_3O^+$), followed by a transfer of $H^+$ from the oxonium ion to an adjacent $H_2O$ molecule, which also must rotate to accept the $H^+$ ion. After the rotation, a new hydrogen bond is formed between the $H^+$ ion and $H_2O$ molecule, breaking the previous hydrogen bond. This new oxonium ion then rotates, allowing another $H^+$ ion to be transferred, continuing the hopping mechanism. For the hopping of an $H^+$ ion in $H_2O$ to an adjacent $OH^-$ ion, a similar process occurs, but with a higher activation energy. Similar processes occur in $D_2O$ (Tada et al., 1992, 1993).

1.4.2.2 Temperature and Pressure Effects

Since the pioneering work by Noyes et al. (1904, 1907, 1908) many other authors have measured values of $\Lambda^\circ$ for a variety of species as a function of temperature and pressure (Mesmer et al., 1988; Zimmerman et al., 1993, 1995, 2002, 2007, 2009; Bianchi et al., 1994; Gruszkie wicz and Wood, 1997; Ho et al., 2000a, 2000b, 2001; Sharygin et al., 2001; Hnedkovsky et al., 2005). Measurements by a variety of different authors have shown that values of transference numbers, $t_i^\circ$ (which can be used to calculate values of
Figure 1.9. The Grotthuss ("proton hopping") mechanism based on the one reported by Tada et al. (1993) and Agmon (1995). Open circles (○) represent oxygen atoms, filled circles (●) represent hydrogen atoms, solid lines (——) represent hydrogen-oxygen bonds, and dashed lines (-----) represent hydrogen bonding.


\( \lambda^\circ \), do change as a function of temperature (Allgood et al., 1940; Allgood and Gordon, 1942; Smith and Dismukes, 1963, 1964; Kay and Vidulich, 1970). However, no known values exist above 388 K. Smith and Dismukes (1963, 1964) have found that there is a linear correlation for \( t_i^\circ \) as a function of temperature:

\[
\log \left[ \frac{1-t_i^\circ}{t_i^\circ} \right] \text{ vs. } \left( \frac{1000}{T} \right)
\]

where \( T \) is in K, which is due to a temperature-independent difference in the activation energies of the transport of species i and j (shown in Figure 1.10 below). These results are consistent with Erying’s (1936) and Taylor’s (1938) discussions of the transport of ions through a medium, where “holes” within the solvent provide an optimal route for ion diffusion by an energy of activation process.

There have been multiple attempts since the 1960’s to model values of \( \lambda^\circ \) and \( \Lambda^\circ \) as a function of temperature, density and viscosity. Quist and Marshall (1965) have used the linear correlation of \( \log[(1 - t_i^\circ)/t_i^\circ] \) vs. \( 1000/T \), from Smith and Dismukes (1963, 1964) data for Na\(^+\), to predict values of \( \lambda^\circ \) for single ions up to 673 K. Marshall (1987a, 1987b) discovered that values of \( \Lambda^\circ \) for salts approach a limiting value at a high density. Smolyakov and Veselova (1975) and Zimmerman et al. (2007, 2009) have shown that values of \( \Lambda^\circ \) could be described as a function of \( \eta_{H2O} \):

\[
\Lambda^\circ = A_1 \cdot (\eta_{H2O})^{-\alpha_2},
\]

where \( A_1 \) and \( A_2 \) are adjustable parameters. Equation (1.44) has very recently been expanded upon to include a density term (Zimmerman et al., 2012a, 2012b):

\[
\log[\Lambda^\circ] = \log[A_1] + \left( A_2 + \frac{A_1}{\rho_{H2O}} \right) \cdot \log[\eta_{H2O}]
\]
Figure 1.10. Linear correlation of $\log[(1 - t^\circ_e)/t^\circ_e]$ vs. $1000/T$ for Na$^+$ in H$_2$O, from Smith and Dismukes (1963, 1964).
Oelkers and Helgeson (1988, 1989) have shown that values of $\lambda^o$ for ions of the same charge could be approximated using linear functions of the standard partial molal entropies of those ions, which can be predicted from the HKF model (Helgeson et al., 1981).

1.4.2.3 Deuterium Isotope Effects

Values of limiting ionic conductivities and transport numbers in D$_2$O vs. H$_2$O have been measured at near-ambient conditions by Longsworth and MacInnes (1937), Swain and Evans (1966), Broadwater and Evans (1974), Nakahara et al. (1985), Ueno et al. (1987, 1990, 1996) and Tada et al., (1992). Swain and Evans (1966) and Broadwater and Evans (1974) have also calculated values of Walden product ratios, $R^\text{Walden}_{\text{D/H}}$, in D$_2$O vs. H$_2$O at 298.15 K:

$$R^\text{Walden}_{\text{D/H}} = \frac{(\lambda^o \cdot \eta)_{\text{D}_2\text{O}}}{(\lambda^o \cdot \eta)_{\text{H}_2\text{O}}} \quad (1.46)$$

Equations (1.41) and (1.46) can be combined, and $R^\text{Walden}_{\text{D/H}}$ can be used as a means of probing the differences of ion-solvent interactions in D$_2$O vs. H$_2$O as a function of temperature and pressure:

$$R^\text{Walden}_{\text{D/H}} = \frac{R_{\text{stokes,H}_2\text{O}}}{R_{\text{stokes,D}_2\text{O}}} \quad (1.47)$$

where $R_{\text{stokes}}$ is the effective Stokes radius of the ion in solution, which is the product, $r_i \cdot f_B$, in equation (1.41). Assuming that $r_i$ is the same whether the ion is in D$_2$O or H$_2$O, $R_{\text{stokes}}$ becomes dependent upon $f_B$, which is what is used to define the relative extent of ion-solvent interactions in D$_2$O vs. H$_2$O. At 298 K, all known values of $R^\text{Walden}_{\text{D/H}}$ appear
either at or near unity, which indicates that there are only small differences between ion-solvent interactions in D\textsubscript{2}O vs. H\textsubscript{2}O (Swain and Evans, 1966; Broadwater and Evans, 1974).

Work has also been done to investigate differences in ionic conductivity of D\textsuperscript{+} vs. H\textsuperscript{+} and OD\textsuperscript{-} vs. OH\textsuperscript{-}. Measurements of values of \Lambda\textsuperscript{0} for DCl and KOD have been made by Longsworth and MacInnes (1937), Gierer and Writz (1952) and Tada et al. (1992, 1993). Those have been used to calculate values of \lambda\textsuperscript{0} for D\textsuperscript{+} and OD\textsuperscript{-}. At near ambient conditions, it has been concluded by Conway et al. (1956) that ratios of values of \lambda\textsuperscript{0} for D\textsuperscript{+} to values of \lambda\textsuperscript{0} for H\textsuperscript{+}, \((\lambda_{D^{+}})\textsuperscript{0}/(\lambda_{H^{+}})\textsuperscript{0}\), should be equal to the square root of the mass ratio of the two isotopes, \(2^{1/2}\). Experimental values of \((\lambda_{D^{+}})\textsuperscript{0}/(\lambda_{H^{+}})\textsuperscript{0}\) approximately equal to \(2^{1/2}\) have been found by Tada et al. (1992) at near ambient conditions. \textit{Ab initio} calculations by Sluyters and Sluyters-Rehback (2010) have also shown that deuterium isotope effects on values of \((\lambda_{D^{+}})\textsuperscript{0}/(\lambda_{H^{+}})\textsuperscript{0}\) are temperature dependent, due to both the Grotthuss mechanism and tunneling effects.

1.5 High Temperature Experimental Methods for Ionization Constant Measurements

1.5.1 Solubility Measurements

Studies of soluble and sparingly soluble salts in aqueous media have been used to measure ionization constants (Marshall, 1985). Such studies require accurate activity coefficient models to distinguish between ion-ion interactions and distinct chemical species. Marshall (1985) reviews methods that have been used to determine the solubility of salts in aqueous media above 373 K. Small high-pressure vessels are used to heat the
solid-liquid equilibrium mixtures. Fitted capillary tubes and valves are attached to the vessels, which are used to sample the solution phases for analytical analysis.

For example, solubility measurements of sulfate salt systems (Lietzke and Stoughton, 1961, 1963) have been used to determine ionization constants for bisulfate, HSO$_4^-$.

Bisulfate ionizes according to the following reaction:

\[
\text{HSO}_4^- (aq) \rightleftharpoons \text{SO}_4^{2-} (aq) + \text{H}^+ (aq)
\]  

(1.48)

By measuring the solubility of a sulfate salt system (such as Ag$_2$SO$_4$(s)) in solutions of H$_2$SO$_4$(aq) of varying concentration, equilibrium concentrations of SO$_4^{2-}$(aq), H$^+$(aq) and HSO$_4^-$(aq) are calculated, which are used to calculate an equilibrium quotient, $Q_a$, for reaction (1.48). Values of $K_a$ are calculated from $Q_a$ and the total ionic strength of the solution, $I$, using the extended Debye-Hückel equation:

\[
\log[Q_a] = \log[K_a] + \frac{A_{\text{DH}} \cdot \sqrt{I}}{1 + (B_{\text{DH}} \cdot \hat{a}) \cdot \sqrt{I}} + B' \cdot I + C' \cdot I^2,
\]  

(1.49)

where $B'$ and $C'$ are adjustable empirical parameters.

The first known measurements of ionization constants, $K_a$, in D$_2$O at elevated temperatures came from Lietzke and Stoughton (1963), when they calculated ionization constants for DSO$_4^-$, from the solubility of Ag$_2$SO$_4$ in solutions of D$_2$SO$_4$. To do this, Lietzke and Stoughton compared the measured concentrations of dissolved Ag$_2$SO$_4$ in solution to the mass of solid Ag$_2$SO$_4$ remaining un-dissolved in the D$_2$SO$_4$. Values of $K_a$ for DSO$_4^-$ were subsequently calculated from equilibrium quotients for DSO$_4^-$ and the total ionic strength of the Ag$_2$SO$_4$/D$_2$SO$_4$ solution.

Measurements of transition metal solubility as a function of pH, discussed previously, have been used to calculate solubility quotients for metals, M$^{2+}$, and their
hydrolyzed species, according to generalized forms of reaction (1.2) and equations (1.3) to (1.4). These measurements have been performed by using experimental set-ups consisting of high-temperature high-pressure feed systems, connected to flow-beds containing a metal oxide. The feed system contains aqueous solutions of HCl or NaOH, saturated with H₂(g), which is passed through the oxide bed, and the resulting dissolved metal is precipitated in a condenser for analysis (Sweeton and Baes, 1970; Tremaine and LeBlanc, 1980; Ziemniak et al., 1995).

When measuring these solubilities as a function of pH, there are several limitations that need to be considered. Due to the pH dependence of metal oxide and hydroxide solubility, the equilibrium pH must be accurately known at elevated temperature and pressure conditions, which, for reasons discussed in more detail below, are difficult to measure. Low solubilities of the hydrolyzed species at elevated temperatures can also make it difficult to accurately measure the concentration of metal ions in solution, since the concentrations may exist below detection limits. Finally, equilibrium between the solid, dissolved species and hydrogen must be demonstrated, which may take a long time to establish (Baes and Mesmer, 1976, 1981; Tremaine and LeBlanc, 1980).

Studies of sparingly soluble salt solubility as a function of ligand concentration have been used to calculate complexation constants (Seward, 1981). By measuring the solubility of a solid as a function of electron donor concentration, metal complex formation constants can be calculated. Early measurements of these types were made in sealed glass tubes inside pressure vessels (Barnes, 1979; Seward, 1981), while more
recent measurements have used flow-through autoclaves (Stefánsson and Seward, 2003a, 2003b; Tagirov and Seward, 2010).

1.5.2 Electromotive Force (EMF) and Potentiometry Measurements

High-temperature high-pressure hydrogen-electrode concentration cells (HECC) for accurate pH measurements were developed at Oak Ridge National Laboratory (Mesmer et al., 1997) and have been in use since the 1970’s. From the difference in the potential between the solution of interest and a reference solution, the equilibrium molality, $m_{H^+}$, is calculated relative to that of the reference cell:

$$H_2, \text{Pt} \mid m_{H^+, \text{NaCl}}, m_{\text{NaCl}} \parallel m_{H^+, \text{test}} \mid H_2, \text{Pt}$$

$$\text{test cell} \quad \text{reference cell}$$

$$\Delta E = E - E^\circ = -\frac{R \cdot T}{F} \cdot \ln \left[ \frac{a_{H^+, \text{test}}}{a_{H^+, \text{reference}}} \right] - E_{ij}$$

$$= -\frac{R \cdot T}{F} \cdot \ln \left[ \frac{m_{H^+, \text{test}} \cdot \gamma_{H^+, \text{test}}}{m_{H^+, \text{reference}} \cdot \gamma_{H^+, \text{reference}}} \right] - E_{ij},$$

where $E_{ij}$ is the junction potential, $E$ is the potential of the test cell and $E^\circ$ is the potential of the reference cell. A pinhole connecting the two cells allows the pressure of hydrogen to be the same and a strong electrolyte (such as NaCl) is used to keep the ionic strength of both cells the same. Both flow and static (batch) HECC cells have been designed, to be capable of making measurements at temperatures up to 573 K. The method is limited to temperatures less than 573 K because response slopes, with a Nernstian value of $\ln[10] \cdot R \cdot T / F$, have been shown not to exist at more elevated temperatures (Midgley, 1990; Mesmer and Holmes, 1992; Lvov and Palmer, 2004).
Reported measurements of $pK_a$ in D$_2$O under hydrothermal conditions came from the works of Shoesmith and Lee (1976) and Mesmer and Herting (1978), using EMF hydrogen concentration cells to study the ionization of D$_2$O and D$_2$PO$_4^-$. In their measurements, values of $m_{H^+} \text{test}$ in equation (1.51) were calculated from measured values of $\Delta E$, which were subsequently used to calculate values of $K_a$.

The yttria-stabalized zirconia (YSZ) electrode is another pH electrode that can be used at elevated temperatures. The YSZ electrode consists of a ZrO$_2$ (8-17% Y$_2$O$_3$) ceramic tube, containing a metal-metal oxide (M$_X$O$_Y$) reference electrode, that conducts electricity through the movement of oxide ions (Midgley, 1990; Macdonald et al., 1992). The potential of the ZrO$_2$ electrode depends only on the standard potential of the M$_X$O$_Y$ reference electrode, $E_{M_XO_Y}^\circ$, at a particular pH and activity of H$_2$O, $a_{H2O}$. Therefore, if $a_{H2O}$ and $E_{M_XO_Y}^\circ$ are known, pH can be determined, according to equation (1.52):

$$
E = E_{M_XO_Y}^\circ - \frac{R \cdot T}{2 \cdot F} \cdot \ln[a_{H2O}] - \frac{2.303 \cdot R \cdot T}{F} \cdot \text{pH}
$$

(1.52)

The YSZ electrode is usually used with the silver-silver chloride (Ag|AgCl) reference electrode (Midgley, 1990; Mesmer and Holmes, 1992; Macdonald et al., 1992; Lvov and Palmer, 2004). Silver-silver chloride electrodes have been used at temperatures up to 548 K, but only for short periods of time due to the solubility of AgCl at elevated temperatures.

To produce more stable reference electrodes for high-temperature pH measurements, pressure-balanced low-temperature reference (PBLTR) electrodes have been used. PBLTR electrodes contain an inner Ag|AgCl electrode, maintained at ambient temperature. The liquid junction between the reference and pH electrode is a teflon tube that contains a KCl electrolyte solution. It is deformable, to account for volume changes.
on pressurization. The liquid junction includes a thermal electric potential due to the large temperature gradient between the cell and reference electrode. If a PBLTR electrode is calibrated using a reference electrode, where the concentration of KCl within the reference electrode and the PBLTR electrode are the same, then the thermal liquid junction potential becomes zero (Macdonald et al., 1992).

1.5.3 UV-Visible Spectroscopy

UV-visible spectroscopy has been used since the 1960’s to determine complexation constants for aqueous transition metal solutions as a function of temperature. For example, Lüdemann and Franck (1967, 1968) measured absorption spectra for nickel and cobalt halides to temperatures of 573 K. Seward and co-workers (Seward, 1984; Heinrich and Seward, 1990; Suleimenov and Seward, 2000; Müller and Seward, 2001) measured absorption spectra for aqueous iron, tin, lead and manganese chloride species to 573 K. Trevani et al. (2001) measured copper(II)-ammonia complex formation equilibria to 523 K. Newton and Swaddle (1974) investigated the decomposition of amine cobalt(III) complexes to temperatures of 423 K.

Measurements under hydrothermal conditions usually consist of placing a pressurized flow cell, mounted within a small oven, within the sample compartment of a commercially purchased UV-Visible spectrometer. Sapphire windows with gold or teflon gaskets contain the pressure and allow UV-Visible measurements to take place (Xiang and Johnston, 1994; Chlistunoff and Johnston, 1998; Trevani et al., 2001; Bulemela et al., 2005; Bulemela and Tremaine, 2009).
Values of $K_a$ for acids and organic colorimetric indicators have also been measured using UV-Visible spectroscopy at high temperatures and pressures (Xiang and Johnston, 1994; Bennett and Johnston, 1994; Chlistunoff and Johnston, 1998; Bulemela et al., 2005; Bulemela and Tremaine, 2009). Absorbance spectra are obtained for the indicator in both the pure acidic and pure basic state, which are compared to spectra for the partially ionized indicator (where the extent of ionization is controlled using buffers). A buffer is chosen which has values of $pK_a$ (as a function of temperature) that overlap with the colorimetric indicator’s values of $pK_a (± 1)$. Examples are presented in Appendix Figure A.1.

Bulemela and Tremaine (2009) reported values of $pK_a$ in D$_2$O for the colorimetric indicator, $\beta$-naphthol, and boric acid. Before their work, D$_2$PO$_4^-$ was the only known acid with accurately measured values of $pK_a$ in D$_2$O under hydrothermal conditions (Mesmer and Herting, 1976). Therefore, Bulemela and Tremaine used the buffer D$_2$PO$_4^-/DPO_4^{2-}$ to define the pH and measured the extent of ionization of $\beta$-naphthol (NapOD in D$_2$O). Values of $pK_a$ for the boric acid buffer in D$_2$O (B(OD)$_3/B(OD)_4^-$) were measured, using the ionization constants and spectra of NapOD to measure the equilibrium values of $n_{D^+}$.

1.5.4 Raman Spectroscopy

Pioneering Raman measurements under hydrothermal conditions were reported by Irish et al. (1982), where thick-walled Pyrex® tubes (used to hold the samples) were pressurized and housed within an oven system, capable of reaching 573 K. Similar studies by Rudolph et al. (1997, 1999) used sealed tubes to measure Raman spectra at saturation pressure.
Protonated (A-H) and unprotonated (A-) weak acids have different vibrational frequencies, \( \nu \), due to differences in the reduced mass (see Section 1.3.1). To determine ionization constants, measurements of integrated intensity, \( I_\nu \), for the vibrational modes are used to find ratios of molalities of unprotonated:protonated species, which are then used to calculate values of \( K_a \):

\[
\frac{m_{A}}{m_{A-H}} = \frac{\sigma_{A-H}^{\nu} I_{A-H}^{\nu}}{\sigma_{A}^{\nu} I_{A}^{\nu}},
\]

(1.53)

where \( \sigma^{\nu} \) is the Raman scattering cross section of the species.

Raman measurements have been used to measure ionization and complexation equilibria, both at low temperatures and under hydrothermal conditions. For example, Dawson et al. (1986) and Knopf et al. (2003) have measured the degree of dissociation of HSO\(_4\)^-, which were then used to calculate equilibrium quotients, \( Q \). These measurements have been made up to temperatures of 523 K. Rudolph (2010) has measured the degree of dissociation for phosphoric acid in H\(_2\)O and D\(_2\)O at 296 K. Rudolph et al. (1997, 1999, 2003) have used Raman spectroscopy to probe hydration, complex-ion formation and ion-pair formation for aqueous solutions of ZnSO\(_4\), FeSO\(_4\) and MgSO\(_4\) at temperatures up to 629 K. More recent advances using diamond anvil cells can be used for measurements up to 1473 K and 2.5 GPa (Bassett et al., 1993).

Raman spectroscopy has been used to measure deuterium isotope effects. Irish and Puzic (1981) have measured values of \( I_\nu \) for nitric acid in D\(_2\)O vs. H\(_2\)O and Gillespie and Robinson (1962) have measured values of \( I_\nu \) for various sulfuric and sulfonic acids in D\(_2\)O vs. H\(_2\)O at elevated temperatures and pressures. A recent publication by Rudolph (2010) has reported a difference in the values of the first ionization constant for phosphoric acid in D\(_2\)O vs. H\(_2\)O at 296 K: \( \Delta pK_a = pK_{a,H2O} - pK_{a,D2O} = 0.28 \).
1.5.5 AC Conductance Measurements

AC conductance is a valuable technique for measuring ionization constants, $K_a$, because it is capable of measuring accurate conductivities of solutions with concentrations as low as $c = 10^{-5}$ mol·L$^{-1}$. In a system that dissociates from a neutral species to a charged species, the concentration of ions is a direct representation of the ionization constant, $K_a$, through the expression:

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-$$

$$(1-\alpha) \cdot c \quad \alpha \cdot c \quad \alpha \cdot c$$  \hspace{1cm} (1.54)

Here, the degree of ionization, $\alpha$, is defined as the ratio of the experimental value of $\Lambda$ for the free ions in solution, $\Lambda^{\text{exp}}$, and the value of $\Lambda$ that HA would have if it were fully dissociated, $\lambda_{\text{H}^+} + \lambda_{\text{A}^-}$, both at the same ionic strength. Values of $\alpha$ are then used to calculate values of $K_a$ (Robinson and Stokes, 1965).

The first values of $K_a$ above 373 K, measured from conductivity experiments, were reported by Noyes et al. (1904, 1907, 1908). MacInnes and Shedlovsky (1932) “perfected” the technique at low temperatures, measuring values of $\lambda_{\text{H}^+} + \lambda_{\text{A}^-}$ for the strong electrolytes: NaCl, HCl and NaA, all at the same concentration (Robinson and Stokes, 1965). High-temperature high-pressure measurements in the 1960’s at Oak Ridge National Laboratories used static conductivity cells made of materials capable of handling extreme environments (Quist et al., 1965; Franck et al., 1965). Further measurements by Quist and Marshall (1965) and Marshall (1987a, 1987b) at Oak Ridge National Laboratories have led to the development of semi-empirical extrapolation techniques to predict values of $\lambda_{i}^{\circ}$ at high temperatures from low-temperature data. More recent measurements by Zimmerman et al. (1993, 1995, 2002, 2007, 2009, 2012a,
Ho et al. (2000a, 2000b, 2001) and Hnedkovsky et al. (2005) have used flow cells to measure ionization and association constants.

Modern theories of the treatment of conductivity data (Corti et al., 2004) can be used to describe how conductivity changes as a function of concentration for a large variety of species. The concentration dependence on solution conductivity has already been introduced using the Onsager equation, equation (1.38). Further developments for symmetrical electrolytes have been made by Fernández-Prini (1969, 1973), which is now known as the Fuoss-Hsai-Fernández-Prini (FHFP) Equation. Pitts et al. (1953, 1970) developed a treatment that separates the forces that act on the individual ions. This was later used by Lee and Wheaton (1978a, 1978b) to derive their equation, which was found to apply to both symmetrical and non-symmetrical electrolytes. Bernard et al. (1992) and Turq et al. (1995) developed their Turk-Blum-Bernard-Kunz (TBBK) equation, which uses the mean spherical approximation. In their work, relaxation and electrophoretic contributions are considered independently and are used to describe the effects of concentration on the conductivity of non-symmetrical electrolytes, as well as associated electrolytes (Bianchi et al., 2000; Corti et al., 2004).

1.5 Ionic Conductivity in Aqueous Solutions

1.6.1 Solution Resistance and Conductivity

The movement of charge throughout an electric circuit follows Ohm’s law:

\[ V = I_e \cdot R_e, \]

where \( V \) is the measured voltage or potential difference across the resistance, \( R_e \) (in ohms, \( \Omega \)), and \( I_e \) is the applied current (in amperes). The specific conductivity of a solution, \( \kappa \),
is determined by the inverse of the solution resistance, $R_s$; the distance between the electrodes, $d$; and the surface area of the electrodes, $A_s$:

$$\kappa = \frac{d}{A_s \cdot R_s} \quad (1.56)$$

The ratio, $d/A_s$, is defined as the cell constant ($k_{cell}$), and has units of cm$^{-1}$. It is measured using standard solutions of KCl(aq) in H$_2$O. This will be discussed in more detail in Chapter 2. According to equation (1.56), $\kappa$ has units of S·cm$^{-1}$ (or Ω$^{-1}$·cm$^{-1}$). In solution, $\kappa$ is dependent upon the concentration of ions in solution, $c$, and their charge. The molar conductivity, $\Lambda$, for a 1:1 electrolyte is related to $\kappa$ through the concentration, $c$:

$$\Lambda = \frac{\kappa}{c} \quad (1.57)$$

### 1.6.2 Impedance Measurements, the Equivalent Circuit and Calculation of Solution Resistance

A conductivity cell consists of two oppositely polarized plates, separated by an interior space containing the solution. Figure 1.11 below shows a general diagram of such a cell. The application of an alternating current (AC) between the two plates will induce current flow through the circuit, allowing the measurement of solution conductivity (Robinson and Stokes, 1965; Bard and Faulkner, 2001). In an AC circuit, $I_e$ and $V$ in equation (1.55) are out of phase, by a phase angle, $\phi$. Therefore, the conductivity cell does not behave as a resistor, but as a complex impedance circuit with capacitance, resistance and inductance components, which must be represented in terms of impedance, $Z$:

$$Z = Z_{Re} - j \cdot Z_{Im}, \quad (1.58)$$
Figure 1.11 General schematic of a conductivity cell. 1, An alternating current source designed to induce a potential within a solution; 2, An RCL meter designed to measure the frequency-dependent AC impedance across the cell; 3, Solution flow between the plates.
where $Z_{Re}$ is the real component, $Z_{Im}$ is the imaginary component (which contains the inductance) and \( j = (-1)^{1/2} \). The ratio between the real and imaginary components of the impedance is represented by equation (1.59):

$$\tan \phi = \frac{Z_{Im}}{Z_{Re}} = \frac{X_c}{R_c}$$

(1.59)

where $R_c$ is the total resistance and $X_c$ is the capacitive reactance, defined as:

$$X_c = \frac{1}{\omega \cdot C}$$

(1.60)

Here, $\omega$ is the angular frequency ($\omega = 2 \cdot \pi \cdot f$, with $f$ being the original frequency of the alternating current).

Common practice in AC conductance studies is to represent the impedance of the cell by an equivalent circuit, where the resistors and capacitors represent various electrochemical and transport processes that are occurring within the cell. As shown in Figure 1.12 below, an equivalent circuit for a typical cell consists of 6 components (Park et al., 2006). $C_D$ is the double layer capacitance, and is caused by the build up of net opposite charge in solution near the electrode. $C_{cell}$ is the cell capacitance, associated with the two electrodes and various cell components, such as leads. $R_{ct}$ is the charge-transfer resistance, caused by oxidation and reduction reactions that occur near the electrode surfaces. $R_s$ is the actual solution resistance, which is what we seek to measure. Finally, $W$ is the Warburg impedance, which is the limiting ion mobility/mass transfer term. The Warburg impedance is comprised of two components, $a_W$ and $C_l$, which are the fraction pure capacitance associated with the electrodes and the capacitance at zero frequency, respectively (Bard and Faulkner, 2001).
Figure 1.12  An equivalent circuit, based on the one reported by Park et al. (2006). $C_D$, Double layer capacitance; $C_{cell}$, Cell capacitance; $R_{ct}$, Charge transfer resistance; $R_s$, Solution resistance; $W$, Warburg impedance (containing $\alpha_W$ and $C_1$).
$Z_{Re}$ and $Z_{Im}$ measurements are taken at each value of $\omega$ and plotted with respect to each other to form a Nyquist plot, $Z_{Im}$ vs. $Z_{Re}$ (Bard and Faulkner, 2001). In general, a Nyquist plot for a solution (shown in Figure 1.13 below) will consist of a high-frequency region and a low-frequency region. The high-frequency region is semi-circular shaped, crossing the x-axis at $R_s$ and $R_s + R_{ct}$. The low-frequency region will be dominated by the Warburg impedance (where mass transfer control exists), and crosses the x-axis at $R_s + R_{ct} - 2\sigma^2C_D$, where $\sigma$ is based on the diffusion rate of the ions to and from the double layer, and is approximately equal to zero. Therefore, $R_s + R_{ct} - 2\sigma^2C_D$ is approximately equal to $R_s + R_{ct}$. At higher values of $\omega$, ionic mobility does not contribute to the impedance very much, so that the components of the equivalent circuit that must be considered at high values of $\omega$ are $R_s$, $C_D$, and $R_{ct}$. $C_D$ is the only term that represents the imaginary component, $Z_{Im}$, and it approaches zero as $Z_{Im}$ is extrapolated to zero. The result is a value of $R_{ct} + R_s$ at $Z_{Im} = 0$. At low values of $\omega$, ion transport dominates the impedance because the slow change of polarity on the electrodes does not allow for a rapid movement of charge. Therefore, the three primary components of the equivalent circuit that must be considered are $W$, $C_D$, and $R_{ct}$. The extrapolation of the Warburg curve in Figure 1.13 yields $R_s + R_{ct}$.

Experimentally, the Warburg impedance is affected by the nature of the electrode. A linear fit of the low-frequency region in Figure 1.13 will give a representation of the Warburg line. According to equation (1.59):

$$\tan \phi = \frac{Z_{Im}}{Z_{Re}} = m_W, \quad (1.61)$$

which can be rearranged to give:
Figure 1.13  General Nyquist Plot (plot of $Z_{Re}$ vs. $Z_{Im}$) for a solution. The dotted lines (····) show the extrapolations to $R_s$ and $R_s + R_{ct}$.
\[ \phi = \tan^{-1}(m_W), \quad (1.62) \]

where \( m_W \) is defined as the slope of the Warburg line. A pure capacitor has only an imaginary resistance component, \( \phi = \pi/2, \) or 90°. The solid electrode will not behave as a pure capacitor. Therefore \( \phi \) can be defined as:

\[ \phi = \alpha_W \cdot \left( \frac{\pi}{2} \right), \quad (1.63) \]

with \( \alpha_W \) representing the fraction of pure capacitance associated with the electrodes. In order to determine the capacitive effect of the electrode, \( \alpha_W \) must be calculated:

\[ \alpha_W = \phi \cdot \left( \frac{2}{\pi} \right) = Tan^{-1}(m_W) \cdot \left( \frac{2}{\pi} \right) \quad (1.64) \]

Assuming that measurements performed on the solutions and their respective solvents result in the same values of \( R_{ct}, C_D \) and \( C_{cell} \), extrapolation of the Warburg line to \( Z_{Im} = 0 \) can be taken to be approximately equal to \( R_s \) (Hnedkovsky et al., 2005). Figures 1.14 and 1.15 below show Nyquist plots for a solvent (H\(_2\)O) and solute (KH\(_2\)PO\(_4\), \( m = 1.328 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \)) at 374.22 K, with impedance measurements made at the following frequencies: 100, 200, 500, 800, 1000, 2000, 4000, 6000, 8000, and 10 000 Hz. Extrapolations to \( R_s + R_{ct} \) and \( R_s + R_{ct} - 2 \cdot \sigma^2 \cdot C_D \) for H\(_2\)O and KH\(_2\)PO\(_4\), respectively, are also shown in the plots.

### 1.6.3 The Hnedkovsky Extrapolation Method and Calculation of Solution Resistance

In aqueous solutions, the Warburg component to the impedance dominates over other elements of the equivalent circuit. By assuming that the other components to the equivalent circuit are negligible, values of \( R_s \) can be calculated from expressions based on
Figure 1.14  Nyquist Plot (plot of $Z_{Re}$ vs. $Z_{Im}$) for H$_2$O at 374.22 K. Comparison of experimental (●) and predicted (—) impedance data. The dotted line (····) shows the extrapolation along the semi-circle to $Z_{Im} = 0$, where $Z_{Re} = R_s + R_{ct}$.
Figure 1.15  Nyquist Plot (plot of $Z_{Re}$ vs. $Z_{Im}$) for KH$_2$PO$_4$ in H$_2$O at 374.22 K. Comparison of experimental (●) and predicted (---) impedance data. The dotted line (·····) shows the extrapolation along the Warburg line, to the white point, (⊙), $R_s + R_{ct} - 2 \cdot \sigma^2 \cdot C_D$. 

$Z_{lm}$

$Z_{Re}$

$R_s + R_{ct} - 2 \cdot \sigma^2 \cdot C_D$
the Warburg term. Past methods to find values of $R_s$ have extrapolated impedance data to infinite frequency (Noyes et al., 1904, 1907, 1908; Robinson and Stokes, 1965):

$$Z_{Re} = R_s + \frac{b}{f^{1/2}}$$

(1.65)

using $b$ as an adjustable parameter. Using the method of Hnedkovsky et al. (2005), replacing the “1/2” in equation (1.65) with the value of $\alpha_W$ is equivalent to an extrapolation to $Z_{Im} = 0$ along the Warburg line:

$$Z_{Re} = R_s + \frac{b}{f^{\alpha_W}}$$

(1.66)

Given equation (1.66), it is apparent that $Z_{Re}$ approaches $R_s$ as $f^{\alpha_W}$ approaches infinity.

Figure 1.16 below shows a comparison of an extrapolation of impedance data to calculate the values of $R_s$ for a solution of $m = 1.328 \cdot 10^{-4}$ mol·kg$^{-1}$ KH$_2$PO$_4$ in H$_2$O at 374.22 K. Figure 1.16a uses the equivalent circuit method described above (as shown in Figure 1.15 above), and Figure 1.16b uses the method reported by Hnedkovsky et al. (2005). The values of $R_s = (1693.67 \pm 0.9)$ Ω from the equivalent circuit extrapolation method and $R_s = (1693.12 \pm 0.7)$ Ω from the Hnedkovsky extrapolation method agree to within the combined experimental uncertainty.

For solvents, where the Warburg impedance is minimal, Hnedkovsky et al. (2005) suggest that an extrapolation of $Z_{Re}$ to zero frequency be used. This method is recommended because the extrapolation to zero and infinite frequency for a solvent yield very similar values of $Z_{Re}$. Measured values of $Z_{Re}$ at the three lowest measured frequencies are chosen and are extrapolated to $f = 0$, according to equation (1.67):

$$Z_{Re} = R_s + b \cdot f^2$$

(1.67)
Figure 1.16  Comparison of methods used to extrapolate solution impedance data to the real solution resistance, $R_s$. a) equivalent circuit fit extrapolation, and b) the Hnedkovsky et al. (2005) extrapolation, equation (1.66). Comparison of experimental (●) and predicted (—) impedance data for $m = 1.328 \cdot 10^{-4}$ mol·kg$^{-1}$ KH$_2$PO$_4$ in H$_2$O at 374.22 K. The dotted line (····) shows the extrapolation along the Warburg line, to the white point, (○), $R_s$. 
1.6.4 The Fuoss-Hsai-Fernández-Prini Equation

In dilute solutions, the effect of concentration on molar conductivity has been empirically represented by equation (1.38), the Onsager equation (Onsager, 1927), where $S$ is the limiting slope, defined by equations (1.68) to (1.70):

\[ S = \alpha_F \cdot \Lambda^\circ + \beta_F \]  

\[ \alpha_F = \frac{z^2 \cdot e^2 \cdot k}{3 \cdot (2 + 2^{1/2}) \cdot \varepsilon_w \cdot k_b \cdot T \cdot c^{1/2}} = \frac{(82.046 \cdot 10^4) \cdot z^2}{(\varepsilon_w \cdot T)^{3/2}} \]  

\[ \beta_F = \frac{z^2 \cdot e \cdot F \cdot k}{3 \cdot \pi \cdot \eta_w \cdot c^{1/2}} = \frac{(82.487) \cdot z}{\eta_w \cdot (\varepsilon_w \cdot T)^{1/2}}, \]  

where $k$ is defined as the reciprocal radius of the ionic atmosphere (defined below), $z$ is the absolute value of the charge on the ions from the ionized electrolyte, $\eta_w$ is the viscosity of the solvent and $\varepsilon_w$ is the dielectric constant of the solvent (Onsager, 1927).

Equation (1.68) is defined as the limiting law, showing the dependence of $\Lambda$ upon $c$, for an infinitely dilute solution. For non-associated electrolytes, with short-range interactions, higher order contributions to the solution conductivity can be represented by equation (1.71), the Fuoss-Hsai-Fernández-Prini (FHP) equation (Fernández-Prini, 1969):

\[ \Lambda = \Lambda^\circ - S \cdot c^{1/2} + E \cdot c \cdot \ln[c] + J_1 \cdot c - J_2 \cdot c^{3/2} \]  

where:

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

with:

\[ E_1 = \frac{(k \cdot a \cdot b)^2}{24 \cdot c} = \frac{(2.94257 \cdot 10^{12}) \cdot z^6}{(\varepsilon_w \cdot T)^{3/2}} \]
\[
E_2 = \frac{k \cdot a \cdot b \cdot \beta F}{16 \cdot c^{1/2}} = \frac{(4.33244 \cdot 10^5) \cdot z^3}{\eta_w \cdot (\varepsilon_w \cdot T)^2}
\]  
(1.74)

\[
J_1 = 2 \cdot E_1 \cdot \Lambda^o \cdot \left[ \ln \left( \frac{k \cdot a}{c^{1/2}} \right) + \Delta_1 \right] + 2 \cdot E_2 \cdot \left[ \Delta_2 - \ln \left( \frac{k \cdot a}{c^{1/2}} \right) \right]
\]  
(1.75)

\[
J_2 = \frac{k \cdot a \cdot b}{c^{1/2}} \left[ (4 \cdot E_1 \cdot \Lambda^o \cdot \Delta_3) + (2 \cdot E_2 \cdot \Delta_4) \right] - \Delta_5,
\]  
(1.76)

\[
b \cdot a = \frac{(z \cdot e)^2}{\varepsilon_w \cdot k_B \cdot T} = \frac{(16.7099 \cdot 10^4) \cdot z^2}{\varepsilon_w \cdot T}
\]  
(1.77)

\[
k = \left( \frac{4 \cdot \pi \cdot \sum_{i=1}^n e_i \cdot z_i^2}{\varepsilon_w \cdot k_B \cdot T} \right)^{1/2} = \frac{50.2916 \cdot z \cdot c^{1/2}}{(\varepsilon_w \cdot T)^{1/2}}
\]  
(1.78)

\[
\Delta_1 = \frac{1}{b^3} \left[ (2 \cdot b^2) + (2 \cdot b) - 1 \right] + 0.90735
\]  
(1.79)

\[
\Delta_2 = \frac{22}{3 \cdot b} + 0.01420
\]  
(1.80)

\[
\Delta_3 = \frac{0.9571}{b^3} + \frac{1.1187}{b^2} + \frac{0.1523}{b}
\]  
(1.81)

\[
\Delta_4 = \frac{1}{b^3} \left[ (0.5738 \cdot b^2) + (7.0572 \cdot b) - \frac{2}{3} \right] - 0.6461
\]  
(1.82)

\[
\Delta_5 = \frac{E_2 \cdot \beta}{\Lambda^o} \left[ \frac{4}{3 \cdot b} - 2.2194 \right],
\]  
(1.83)

with \(a\) being defined as the Bjerrum distance:

\[
a = \frac{(16.7099 \cdot 10^4) \cdot z^2}{b \cdot \varepsilon_w \cdot T}
\]  
(1.84)

Here, \(b = 2\) and the terms \(J_1\) and \(J_2\) are based upon the electrophoretic (ion movement) effect and the resulting ionic atmosphere relaxation in conductivity. The FHFP equation
is known to be satisfactory at 298.15 K, and can be applied to dilute \((c < 0.01 \text{ mol}\cdot\text{L}^{-1})\), symmetrical electrolytes (Fernández-Prini, 1969, 1973; Bianchi et al., 2000; Corti et al., 2004). For a weak acid, equation (1.71) takes the form:

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

(1.85)

where \(\alpha \cdot c\) is the ionic strength of the partially dissociated electrolyte in solution.

Equation (1.85) can be used to calculate values of \(\alpha\) and \(K_a\) for a weak acid. This will be discussed in more detail in Chapter 2.

### 1.6.5 The Turk-Blum-Bernard-Kunz Equation, and Other MSA Models

The Pitts model (Pitts et al., 1953, 1970; Pethybridge and Taba, 1977; Bianchi et al., 2000) separates individual forces acting on ions, \(i\), in solution:

\[
-z_i \cdot e \cdot X = F_i^{\text{vis}} + F_i^i + F_i^r
\]

(1.86)

\(F_i^{\text{vis}}\) contributes to the dielectric friction and viscous effects (which determines the limiting molar ionic conductivity), \(F_i^i\) is the force that is due to the stress acting on the local field of the ion’s surface and \(F_i^r\) is the force due to electrostatic interactions between the surrounding ions with each other and the ion itself. Lee and Wheaton (Lee and Wheaton, 1978a, 1978b; Bianchi and Fernández-Prini, 1993) used the same strategy as Pitts, using the ionic electrical mobility to calculate the force acting on the ions. The resulting equation is a modified form of equation (1.71), which deals with unsymmetrical electrolytes more appropriately, and still contains the “\(c \cdot \ln[c]\)” term, resulting in calculated values of \(\Lambda^\circ\) similar to those obtained using the FHFP equation.

Another approach that can be used to describe the dependence of \(\Lambda\) on \(c\) is the Turk-Blum-Bernard-Kunz (TBBK) equation, which is a mean spherical approximation.
(MSA) theory based on the approach used by Fuoss and Onsager (Bernard et al., 1992; Turq et al., 1995; Bianchi et al., 2000). Relaxation and electrophoretic contributions are added to Fuoss and Onsager’s equation, resulting in an equation for the ionic molar conductivity:

\[
\lambda_i = \lambda_i^\circ \left(1 + \frac{\partial v_i^\text{el}}{\partial v_i^\circ}\right) \left(1 + \frac{\partial X}{X}\right)
\]  

(1.87)

In equation (1.87), \(v_i^\text{el}\) is the velocity of the ion, \(v_i^\circ\) is the velocity of the ion at infinite dilution and \(X\) is the electric field.

A comparison of Lee and Wheaton, FHFP and TBBK models has been done by Bianchi et al. (2000). This comparison has shown two primary differences between the FHFP model and the TBBK model. The first key difference is that equation (1.87) separates the electrophoretic and relaxation terms, complicating the investigation of aqueous solution conductance as a function of concentration. The second key difference is the lack of the logarithmic “\(c \cdot \ln[c]\)” term in the TBBK model, which is present in the FHFP model, equation (1.71). The term “\(c \cdot \ln[c]\)” does not overestimate values of \(\Lambda^\circ\); which is an essential term needed to calculate values of \(K_a\). Bianchi et al. (2000) have shown that the TBBK model can accurately model the concentration dependence of \(\Lambda\) over a larger concentration range than the FHFP equation at 298.15 K. Moreover, the TBBK model is applicable to unsymmetrical electrolytes at 298.15 K, whereas the FHFP model is not (Bernard et al., 1992; Turk et al., 1995).
1.7 Deuterium Isotope Effects

1.7.1 Aquamolality ($m_{\text{aq}}$) Standard State

The thermodynamic treatment of aqueous solutes requires a Henry’s law standard state defined by an appropriate concentration scale. Various concentration standard state units such as molarity and molality are used. Conductance measurements typically use $c$ as the preferred standard state, because conductivity measurements are based on the surface area ($A$) and the separation distance of the electrodes. However, the complications associated with solution expansion are difficult to treat (Hepler, 1981). Molality, however, is not dependent upon temperature and is therefore a more useful standard state to use over a large range of temperature.

In order to deal with the differences in $c$ and $m$ standard states, solutions are commonly made on the $m$ scale (to keep them temperature independent) and have then been converted to $c$. To calculate values of $c$ from values of $m$, the density of the solution, $\rho$, mass of the solute, $w_2$, and mass of the solvent, $w_1$, must be used as follows (Klotz and Rosenberg, 1972):

$$c = \frac{m \cdot \rho \cdot w_1}{w_1 + w_2},$$

(1.88)

where $\rho$ can calculated from the density of the solvent, the molar mass of the solute, $M_2$, and the partial molar volume, of the solute, $V^\circ$:

$$\rho = \frac{(M_2 \cdot \rho_{\text{H}_2\text{O}} \cdot m) + (1000 \cdot \rho_{\text{D}_2\text{O}} \cdot m)}{(V^\circ \cdot \rho_{\text{H}_2\text{O}} \cdot m) + 1000}$$

(1.89)

To compare the differences in values of $K_a$ in $\text{D}_2\text{O}$ vs. $\text{H}_2\text{O}$ directly, a standard state based on mole fraction is needed (Laughton and Robertson, 1969; Arnett and McKelvey, 1969). Aquamolality, $m_{\text{aq}}$, is defined as the moles of solute per 55.509 moles
of solvent. Introducing this new standard state eliminates the dependence upon mass, density, and volume of the solvent; instead focusing solely on the number of moles of solute and solvent present (which is both solvent type and temperature independent). The use of the aquamolality standard state allows experimental differences in the properties of species in $D_2O$ vs. $H_2O$ to be compared directly. In $H_2O$, there are 55.509 moles of solvent in 1 kg, so $m = m_{aq}$. In $D_2O$, however, there are 49.936 moles of solvent in 1 kg. Therefore, 1.1117 kg of $D_2O$ is needed to have 55.509 moles of $D_2O$, and $m_{aq}$ for solutions in $D_2O$ is defined as follows:

$$m_{aq} = m \cdot \left( \frac{M_{D_2O}}{M_{H_2O}} \right) = m \cdot 1.1117$$  \hspace{1cm} (1.90)

1.7.2 Solvation Effects at 298.15 K

Values of limiting ionic conductivity, $\lambda_i^\circ$, have been used as a tool to explore the nature of ion-solvent interactions as a function of temperature, pressure and ionic radius. Kay and Evans (1966) and Kay (1991) have calculated values of the Walden product, $\lambda_i^\circ \eta_{H2O}$, for many species near ambient conditions. They have found that the presence of ions in aqueous solution causes the properties of the solvent surrounding the ion to differ from those of the bulk, thus affecting values of $\lambda_i^\circ$ in solution.

Secondary deuterium isotope effects for ions have been investigated by comparing values of $\lambda_i^\circ$ for species in $D_2O$ vs. $H_2O$ at near-ambient conditions (Longsworth and MacInnes, 1937; Swain and Evans, 1966; Broadwater and Evans, 1974; Tada et al., 1992). Comparisons of the Walden product for species in $D_2O$ vs. $H_2O$, using the Walden product ratio, equation (1.47), have been reported at 298 K (Swain and
Evans, 1966; Broadwater and Evans, 1974). Gierer and Wirtz (1952) have also measured
the conductance of aqueous solutions of DCl in D₂O to 368.15 K.

There are no known values of λᵢ° in D₂O that have been measured at temperatures
above 373.15 K. However, investigations by Gierer and Wirtz (1952) and Tada et al.
(1992) have shown that ratios of λᵢ° for ions in D₂O vs. H₂O change as a function of
temperature, up to 368.15 K.

1.7.3 Acid/Base Equilibria

Deuterium isotope effects on the ionization constants of acids and bases in D₂O
(pKᵦ,D₂O) vs. H₂O (pKᵦ,H₂O) are measured on the aquamolality standard state scale, for
reasons discussed above in Section 1.7.1, and represented as values of ∆pKᵦ:

\[ \log \left[ \frac{K_{\text{aq,H}_2\text{O}}}{K_{\text{aq,D}_2\text{O}}} \right] = pK_{\text{a,D}_2\text{O}} - pK_{\text{a,H}_2\text{O}} = \Delta pK_{\text{aq}}, \]  \hspace{1cm} (1.91)

where \( K_{\text{aq,D}_2\text{O}} \) is calculated from \( K_{\text{a,D}_2\text{O}} \) using the same conversion factor for \( m_{\text{aq}} \) from \( m \),
equation (1.90). For a simple ionization equilibrium:

\[ \text{DA} \rightleftharpoons \text{D}^+ + \text{A}^- \]  \hspace{1cm} (1.92)

\[ K_{\text{aq,D}_2\text{O}} = K_{\text{a,D}_2\text{O}} \cdot 1.1117 \]  \hspace{1cm} (1.93)

Values of ∆pKᵦ on the molality standard state scale (\( \Delta pK_{\text{a}} = pK_{\text{a,H}_2\text{O}} - pK_{\text{a,D}_2\text{O}} \)) as
a function of pKᵦ,H₂O have been measured extensively at 298.15 K, and have been
compiled by Laughton and Robertson (1969). Figure 1.17 below shows these values of
\( \Delta pK_{\text{a}} \), plotted as a function of pKᵦ,H₂O. By averaging all the values of ∆pKᵦ reported in
Figure 1.17, it has been shown that ∆pKᵦ has an average value of 0.46 ± 0.2 (Laughton
and Robertson, 1969). Figure 1.17 shows this average, with the solid line at the value of
Figure 1.17  Values of $\Delta pK_a$ values vs. $pK_{a,H2O}$ at 298.15 K, from the results tabulated by Laughton and Robertson (1969). (⊙), inorganics (□), aromatics (△), carboxylic acids (×), and amino acids (○). The solid line (——) is at $\Delta pK = 0.46$ and the dashed lines (- - - -) are the deviation of ± 0.2 units.
0.46, and the dashed lines representing the deviation of ± 0.2 units. The data in Figure 1.17 show a remarkable amount of consistency, especially considering the number of different species investigated, over such a large range of $pK_{a,H2O}$. Figure 1.17 also shows that there is a slight increase in $\Delta pK_a$ as a function of $pK_{a,H2O}$. This trend was noted by Halpern (1935), Rule and La Mer (1938), McDougall and Long (1962), Salomaa et al. (1969c) and Paabo and Bates (1970). These authors have discussed this observation in terms of differences in zero-point energies of O-D vs. O-H vibrations.

MacDougall and Long (1962) reported that the trend observed in Figure 1.17 can be represented reasonably well by equation (1.94):

$$\Delta pK_a = 0.41 + (0.02 \cdot pK_{a,H2O}),$$

(1.94)

where the stronger O-D vs. O-H hydrogen bond results in a weaker ionization constant for the deuterated acid and a larger value of $\Delta pK_a$. Bigeleisen and Mayer (1947) and Bigeleisen (1949, 1953, 1955, 1961) have also demonstrated the importance of the changes in zero-point energy of O-D vs. O-H in calculating the relative reaction rates and thermodynamic properties of isotopic molecules.

Although equation (1.94) represents the trend observed in Figure 1.17 reasonably well, it is not exact. MacDougall and Long (1962) and Paabo and Bates (1970) suggested that differences in the acid may be the cause. MacDougall and Long reported that if the acids are grouped according to structural type, then linear lines similar to equation (1.94) exist, but with slopes that are not equal to 0.02. Paabo and Bates reported that inorganic acids have a slope in equation (1.94) that differs from organic acids. Dahlgren and Long (1960), McDougall and Long (1962) and Salomaa et al. (1964, 1969a, 1969b, 1969c) have discussed the effects that hydrogen bonding may play. McDougall and Long stated
that intramolecular hydrogen bonds within acids (such as maleic acid) would cause values of $\Delta pK_a$ to be larger than those predicted by equation (1.94). Perrin and Dong (2007) have also investigated how inductive effects and electron delocalization can affect values of $\Delta pK_a$, stating that secondary isotope effects can affect the acidity of deuterated carboxylic acids and phenols. Also, Salomaa et al. (1964) pointed out that forms of equation (1.94) make reasonable approximations of $\Delta pK_a$ as a function of $pK_{a,H_2O}$ for stronger acids, but not for weaker, monoprotic ones.

Bunton and Shiner (1961) have calculated values of $\Delta pK_a$ for several species by comparing the number and strength of hydrogen bonds to water molecules surrounding reactant and product species. In their work, Bunton and Shiner used the sum of the vibrational frequencies of hydrogen bonds in solution, before and after ionization, to calculate values of $\Delta pK_a$. Their model has shown good agreement with previous experimental work at 300 K (Bunton and Shiner, 1961). Additional theoretical calculations by Swain and Bader (1960) and Marcus and Ben-Naim (1985) have also used differences in water solvation to discuss the deuterium isotope effects. Swain and Bader (1960) and Marcus and Ben-Naim (1985) have also shown that reasonable estimates of vibrational frequencies and thermodynamic properties can be made at 298.15 K.

### 1.7.4 Ionic Transport Properties

As mentioned in Section 1.4.2, multiple authors have measured values of $\lambda_i$ and $t_i$ in D$_2$O at 298.15 K (Longsworth and MacInnes, 1937; Gierer and Writz, 1952; Kay and Evans, 1965; Swain and Evans, 1966; Nakahara et al., 1985; Tada et al., 1992; Ueno,
1996; Biswas and Bagchi, 1997). Investigations by these authors have consistently shown that values of $\lambda_i$ for a species in D$_2$O are less than the corresponding values in H$_2$O, which have been attributed to the increased structural order of D$_2$O, when compared to H$_2$O (reasons for which have been described in Section 1.3.1). Tada et al. (1992) noted that differences in excess D$^+$ vs. H$^+$ conductance, $\lambda_E$ (which is attributed to the Grothuss mechanism, shown in Figure 1.9), can be approximately estimated by the ratio:

$$\frac{\lambda_{E,H}}{\lambda_{E,D}} \approx \left( \frac{M_D}{M_H} \right)^{1/2} = (2)^{1/2}, \quad (1.95)$$

where $M_D$ and $M_H$ are the molar masses of D and H, respectively. Equation (1.95) stems from observations by Conway et al. (1956), that $\lambda_{E,H}$ can be calculated from the expression:

$$\lambda_{E,H} = \frac{1}{9} \cdot k_B \cdot \left( \frac{P}{M_H} \right)^{1/2} \cdot \left( \frac{f_E}{P} \right) \cdot l_T \cdot F, \quad (1.96)$$

where $f_E$ is the force applied by an external field, $l_T$ is the distance the proton is transported by each rotation and transfer, $P$ is the force on the hydrogen-bonded water molecules, caused by H$_3$O$^+$ or OH$^-$ and $F$ is Faraday’s constant (Tada et al., 1992). For D$^+$ in aqueous solution, values of $l_T$, $P$, and $f_E$ are assumed equal to those for H$^+$.

Differences in dielectric friction coefficients for ions in D$_2$O vs. H$_2$O, described by an improved version of the Hubbard-Onsager theory by Ibuki and Nakahara (1986), have been compared by Nakahara et al. (1985) and Ueno et al. (1996). The results have indicated that values of the dielectric friction coefficients are larger for species in D$_2$O, when compared to H$_2$O, which is consistent with a larger viscosity for D$_2$O relative to that of H$_2$O.
As discussed previously in Section 1.4.2, the deviations from the Walden product, equation (1.41), are thought to arise because the properties of the solvent surrounding the ion differ from those of the bulk solvent (Frank and Wen, 1957). Ions that are deemed to be “structure makers” and “structure breakers” change the local solvent sphere around the ion, causing its viscosity to be either higher or lower than that of the bulk solvent, respectively (Kay, 1991; Marcus, 1994, 2009; Jenkins and Marcus, 1995). For “structure making” ions in D$_2$O vs. H$_2$O, at 298.15 K, the solvation shell around the ion in D$_2$O is expected to be more strongly bound, when compared to H$_2$O. Therefore, according to equation (1.47), it is expected that the value of $R_{\text{Walden}}^{D/H}$ for a “structure maker” would be less than unity. “Structure breaking” ions would be expected to break down the ion-localized solvent shell more in D$_2$O vs. H$_2$O. The result would be a value of $R_{\text{Walden}}^{D/H}$ greater than unity. This agrees with Frank and Wen’s (1957) model of ionic hydration in solution. Values reported by Kay and Evans (1965), Swain and Evans (1966), Broadwater and Evans (1974) and Broadwater and Kay (1975) show that values of $R_{\text{Walden}}^{D/H}$ at 298.15 K are near, but not exactly equal to unity for a wide variety of ionic species. According to Swain and Evans (1966), the fact that $R_{\text{Walden}}^{D/H} \approx 1$ is consistent with a modification of the Stokes’ equation presented by Zwanzig (1963), which allows for relaxation of the solvent molecules around the ion.

1.7.5 Temperature and Pressure Effects

Although several authors: Dessauges et al. (1980), Allred and Woolley (1981) and Jákli (2007), have reported apparent and partial molar volumes for strong electrolytes at temperatures below 373.15 K, the only known measurements of these properties above
that 373.15 K are from Trevani et al. (2007). There have also been a few measurements of values of $\Delta pK_{aq}$ on acid-base ionization under hydrothermal conditions. The ionization constant of $D_2O$ was measured using potentiometry by Shoesmith and Lee (1976) and Mesmer and Herting (1978), at temperatures up to 573.15 K. Mesmer and Herting (1978) also measured the second ionization constant of phosphoric acid ($D_2PO_4^-$) up to 573.15 K. Bulemela and Tremaine (2009) used UV-visible spectroscopy to measure values of $\Delta pK_{aq}$ for the colorimetric indicator $\beta$-naphthol (2-naphthol, $C_{10}H_7OD$) and boric acid ($B(OD)_3$), both from 498.15 to 573.15 K. Finally, values of $\Delta pK_{aq}$ for $DSO_4^-$ were reported by Lietzke and Stoughton (1963). Values of $\Delta pK_{aq}$ for $D_2PO_4^-$, $\beta$-naphthol, $B(OD)_3$ and $DSO_4^-$ as a function of temperature are shown in Figure 1.18 below. An expanded version of Figure 1.18 (just showing the experimental data for $D_2PO_4^-$, $\beta$-naphthol and $B(OD)_3$) is shown in Figure 1.19 below. As shown in Figures 1.18 and 1.19, the average of the values of $\Delta pK_{aq}$ at 298 K are $\Delta pK_{aq} \approx 0.55$ for $D_2PO_4^-$, $\beta$-naphthol and $B(OD)_3$. These fall by 0.1 to 0.2 units in $\Delta pK_{aq}$ above 373 K and are then relatively independent of temperature. Values of $\Delta pK_{aq} \approx 0.30$ for $DSO_4^-$ at 298 K, but fall drastically with increasing temperature.

Theoretical models have been developed to describe the temperature dependence of $\Delta pK_{aq}$. Building upon the previous work of Bigeleisen et al. (1947, 1949, 1953, 1955), Mesmer and Herting (1978) have presented a simplified zero-point energy approximation model, where only the O-H chemical bond on the acid is considered to contribute to the difference in ionization of the species in $D_2O (K_{a,D2O})$ vs. $H_2O (K_{a,H2O})$: 
Figure 1.18  Figure of values of $\Delta pK_{aq}$ values vs. $T$ for a variety of species: $\text{D}_2\text{PO}_4^-$ (□), Mesmer and Herting (1978); $\text{DSO}_4^-$ (△), Lietzke and Stoughton (1963); $\beta$-naphthol (◇) and $\text{B(OD)}_3$ (▽), Bulemela and Tremaine (2009).
Figure 1.19  Figure of values of $\Delta pK_{aq}$ values vs. $T$ for a variety of species (expanded version): $\text{D}_2\text{PO}_4^-$ ($\square$), Mesmer and Herting (1978); $\beta$-napthol ($\bigodot$) and $\text{B(OD)}_3$ ($\triangleright$), Bulemela and Tremaine (2009).
$$\log \left[ \frac{K_{a,\text{H}_2\text{O}}}{K_{a,\text{D}_2\text{O}}} \right] = -\frac{h \cdot c_v}{\ln 10 \cdot 2 \cdot k_B \cdot T} \cdot (\Delta v_{\text{O-H}} - \Delta v_{\text{O-D}})$$

$$= -\frac{h \cdot c_v}{2 \cdot \ln 10 \cdot k_B \cdot T} \cdot \Delta v_{\text{O-H}} \cdot \left( 1 - \left( \frac{\mu_{\text{O-H}}}{\mu_{\text{O-D}}} \right)^{1/2} \right)$$

(1.97)

Here, $h$ is Planck’s constant, $c_v$ is the speed of light and $\Delta v$ is the loss of a vibration frequency when the O-D or O-H bond on the acid is broken. Although equation (1.97) was found to be a reasonable estimate for the ionization of $\text{H}_2\text{PO}_4^-/\text{D}_2\text{PO}_4^-$ at 298 and 573 K (Mesmer and Herten, 1978), it ignores the secondary deuterium solvent isotope effect.

The model by Bunton and Shiner (1961) appears to be more realistic, taking into consideration all O-H bonds involved in the reaction, as shown in Figure 1.20. Bunton and Shiner calculate $\Delta pK_a$ as follows:

$$\Delta pK_a = -\log \left[ \frac{K_{a,\text{H}_2\text{O}}}{K_{a,\text{D}_2\text{O}}} \right] = \frac{\sum v_{\text{O-H,reactants}} - \sum v_{\text{O-H,products}}}{12.53 \cdot T},$$

(1.98)

where $v_{\text{O-H,reactants}}$ and $v_{\text{O-H,products}}$ for an acetic acid (as an example), respectively are:

$$\Delta v_{\text{O-H,reactants}} = v_{\text{H,1}} + v_{\text{H,2}} + 5 \cdot (v_{\text{H,3}})$$

(1.99)

$$\Delta v_{\text{O-H,products}} = 4 \cdot (v_{\text{H,4}}) + 3 \cdot (v_{\text{H,5}}),$$

(1.100)

as shown in Figure 1.20. The $5^{th}$ $v_{\text{H,3}}$ in equation (1.99) is from an additional solvent hydrogen bond attached to $\text{H}_2\text{O}$, which is required to keep the number of hydrogen bonds donated and accepted on each side of the reaction the same. To calculate values of $v_{\text{H,1}},$ Bunton and Shiner used the approximation of Gordy and Stanford (1941), who found that O-H stretching frequencies follow an approximately linear dependence on the $pK_a$ of the weak acid. Comparison of the experimental value of $\Delta pK_a$ for acetic acid
Figure 1.20  The O-H stretching frequencies ($\nu_H$) observed on the reactants-side and products-side of the ionization reaction of acetic acid used to calculated values of $\Delta pK_{\text{aq}}$ by Bunton and Shiner (1961). The dashed lines (-----) represent hydrogen bonds.
(ΔpKₐ,exp = 0.52) at 298.15 K, reported by Martin and Butler (1939), and the predicted value of ΔpKₐ (ΔpKₐ,pred = 0.49), calculated from equations (1.98) to (1.100), the Bunton and Shiner model shows excellent agreement. At the time of Bunton and Shiner’s work, no values of ΔpKₐ existed at higher temperatures, so it is not known if equations (1.98) to (1.100) can be used to accurately predict values of ΔpKₐ under hydrothermal conditions.

Before this project, investigations of transport properties in D₂O above 292.15 K had not been reported. However, studies at ambient temperatures have provided useful information about isotope effects on ion solvation (Longworth and MacInnes, 1937; Gierer and Writz, 1952; Kay and Evans, 1965; Swain and Evans, 1966; Nakahara et al., 1985; Ueno et al., 1987, 1990, 1996; Tada et al., 1992, 1993; Ueno, 1996; Biswas and Bagchi, 1997; Sluyters and Sluyters-Rehbach, 2010). Measurements by Gierer and Writz (1952) have shown that differences in λₑ,D° vs. λₑ,H° are temperature sensitive near ambient conditions, but become constant at higher temperatures. Tada et al. (1992) have reported values of λₑ,D° vs. λₑ,H° from 278.15 to 338.15 K and have discussed the deuterium isotope effects on these values using the model of Conway et al. (1956). In their explanation, Tada et al. indicated that with an increase in temperature, breakdown of hydrogen bond strength will cause the pre-rotation of either D₂O or H₂O in Figure 1.9 to be approximately the same as each other, resulting in deuterium isotope effects that depend only upon the root of the mass ratio of D vs. H, which has been described previously, equation (1.95). These explanations are further confirmed by Sluyters and Sluyters-Rehbach (2010), who have also described the transport of D⁺ vs. H⁺ in terms of diffusion, in addition to proton hopping.
1.8 Objectives of Project and Structure of Thesis

My goal in this thesis was to measure deuterium isotope effects on ionization equilibria for weak acids under hydrothermal conditions. At present, only four values of $pK_{\text{aq}}$ in $\text{D}_2\text{O}$ under hydrothermal conditions have been measured. There is a strong need to quantify deuterium isotope effects on ionization equilibria for weak acids under hydrothermal conditions so they can be used to derive methods to predict hydrolysis constants for transition metals in $\text{D}_2\text{O}$, such as those involved in the solubility of $\text{Fe}_3\text{O}_4$, shown in equations (1.1) to (1.6). The measurements reported in this thesis allowed us to expand the current literature and to provide a better understanding of these effects.

In this thesis, we have measured values of $\Delta pK_{\text{aq}}$ for two systems under hydrothermal conditions. Of the methods for measuring values of $\Delta pK_{\text{aq}}$ presented in Section 1.5, AC conductance was chosen as the most suitable technique for study, for several reasons. First is its ability to make accurate measurements on weak acid systems. The experimental design used in this project allowed us to measure the conductivity of solutions of weak acids and the corresponding strong electrolytes under conditions that remove systematic errors, by measuring direct differences between the aqueous solutions in $\text{D}_2\text{O}$ versus $\text{H}_2\text{O}$. Also, by measuring the conductivity of the strong electrolytes in $\text{D}_2\text{O}$ versus $\text{H}_2\text{O}$, we have provided further insight into the nature of secondary deuterium isotope effects under hydrothermal conditions. The experimental conductivity measurements were done jointly, as a collaboration with Dr. Hugues Arcis and Professor Gregory Zimmerman, under Professor Tremaine’s supervision. The calculations and modeling were my work, co-supervised by Dr. Arcis and Professor Tremaine.
Although a large number of near-ambient data have been reported on deuterium isotope effects, no one has investigated these effects under hydrothermal conditions. In this thesis, the deuterium isotope effects on ionization constants were measured for two systems: acetic acid (from 373.15 to 548.15 K) and phosphoric acid (from 298.15 to 573.15 K), both at approximately 20 MPa. The measurements were made on a high-temperature high-pressure AC conductivity flow cell that was originally designed at the University of Delaware, as reported by Zimmerman et al. (1995) and subsequently improved upon by Sharygin et al. (2002) and Hnedkovsky et al. (2005). Acetic acid was chosen as the first system for study because we could compare our values of $pK_{aq}$ for acetic acid in $H_2O$ with literature values reported by Zimmerman and Wood (2002). Phosphoric acid was chosen because its known value of $pK_{aq,H_2O}$ ($pK_{aq,H_2O} = 2.094$) at 298.15 and 20 MPa (Read, 1988) is lower than the known value of $pK_{aq,H_2O}$ of acetic acid ($pK_{aq,H_2O} = 4.76$) at 298.15 MPa and 20 MPa (Zimmerman and Wood, 2002). This is also the case at high temperatures and pressures (Read, 1988; Zimmerman and Wood, 2002). Phosphoric acid was also chosen because known literature of values of $\Delta pK_{aq}$ for $D_2PO_4^-$ existed under hydrothermal conditions, which could be compared (Mesmer and Herting, 1978). In measuring values of $\Delta pK_{aq}$ for systems with different values of $pK_{aq,H_2O}$ under hydrothermal conditions, I have provided fundamental data which can be used to investigate how values of $\Delta pK_{aq}$ as a function of $pK_{aq,H_2O}$ behave at elevated temperatures.

In addition to this introduction, the thesis consists of six more chapters. Chapter 2 contains the experimental methods used to study deuterium isotope effects under hydrothermal conditions. Chapter 3 presents the measurements of deuterium isotope
effects for acetic acid from 373.15 to 548.15 K and Chapter 4 describes similar measurements made for phosphoric acid, from 298.15 to 573.15 K. Chapter 5 focuses on deuterium isotope effects on ionic hydration. Chapter 6 reports a scoping study that I did to predict values of $\Delta pK_{aq}$ as a function of temperature and $pK_{aq,H2O}$. Finally, Chapter 7 consists of conclusions and future research.
2.1 Transfer and the Isotopic Purity of D$_2$O

2.1.1 D$_2$O Source and Isotopic Purity

Accurate measurements of deuterium isotope effects require that D$_2$O be greater than 99 mol % isotopically pure (Arnett and McKelvey, 1969). Isotope exchange studies have shown that at the surface-to-air interface of liquid D$_2$O, an exchange between H and D isotopes from H$_2$O vapor and D$_2$O liquid readily occurs. The result, over an exposure time of 40 hours, can be a decrease in D$_2$O purity, by up to 50 mol % (Deeny and O’Leary, 2009). Therefore, D$_2$O must be carefully protected from ambient air in the preparation of solutions and subsequent experimental work.

The D$_2$O used in this project was donated from Bruce Power (99.85 mol % isotopically pure as shipped), as part of an industrial-based NSERC/UNENE (University Network of Excellence in Nuclear Engineering) grant on solvent isotope effects. The D$_2$O was donated in large quantities of 50 L (contained within 50 L high-density polyethylene, HDPE, carboys) and, in order to be able to use the D$_2$O more easily, it was transferred to 1 L HDPE bottles.

2.1.2 Storage and Handling of D$_2$O

The transfer process was carried out in a large glove-box purged with N$_2$ (g), using the set-up shown in Figure 2.1 below. The carboy was placed inside of the glove-box. A specialty Teflon® cap, which consisted of a tap and “snorkel”, allowed the D$_2$O to be
Figure 2.1  Set up of the D$_2$O transfer process. 1, Glove-box; 2, 1L HDPE bottle filled with D$_2$O and capped; 3, 1 L HDPE bottle filling with D$_2$O; 4, empty HDPE bottle; 5, 50 L HDPE carboy; 6, tap attached to the specialty Teflon© cap; 7, “snorkel” attached to the specialty Teflon© cap; 8, support stands.
poured from the 50 L carboy into the 1 L HDPE bottles in the dry atmosphere of the glove-box. The carboy rested on top of two support stands, which were raised and lowered, to assist with pouring. After each bottle was filled, it was sealed with a lid in order to keep the D$_2$O within the bottle under an N$_2$(g) environment.

All transfers of the D$_2$O used in solution preparation and experimental measurements were done under Ar(g) environments. Solution preparation was done in a glove bag, purged with Ar(g). Stock solutions were prepared in HDPE bottles and the diluted solutions (which were used for measurements) were stored in Pyrex© bottles, both of which were kept under a slightly positive Ar(g) pressure.

2.1.3 Analyzing the Isotopic Purity of D$_2$O and Measuring the Conductivity of D$_2$O

In order to determine the isotopic purity of the transferred D$_2$O, $^1$H NMR testing was performed, using acetic acid as an internal reference (Goldman, 1957; Kasler, 1973). Two distinguishable singlet peaks for the methyl:acetyl protons, with a ratio of 3:1, are observed for acetic acid. Deuterium, $^2$H, is a quadrupolar nuclei (spin = 1), and has a different magnetic moment from $^1$H, so that $^2$H will not contribute to the $^1$H NMR signals. Protons from the carboxylic group will readily exchange with D, whereas those attached to methyl end will not (Hamann and Linton, 1977). Therefore, in D$_2$O-based solutions of CH$_3$COOD, the concentration of $^1$H present in a sample of D$_2$O as an isotopic impurity is determined by its integrated peak height compared to those of the methyl protons.

In order to calculate the mol % of $^1$H impurities (% impurities) in D$_2$O, the integrated peak ($IP$) ratio of acetyl:methyl protons was needed. The $IP$ ratio was used to
calculate the number of moles of heavy water that contained a proton, \( n_{\text{HOD}} \):

\[
n_{\text{HOD}} = IP \cdot n_{\text{CH3COOD}} ,
\]

(2.1)

where the number of moles of CH\(_3\)COOD (\( n_{\text{CH3COOD}} \)) was calculated using the mass of CH\(_3\)COOD in the solution (weighed to a relative precision of \( \pm 0.2 \% \)) and the molar mass of CH\(_3\)COOD. Because the \(^1\)H in D\(_2\)O is isotopically dilute, the light water impurity in D\(_2\)O would exist as HOD. The number of moles of D\(_2\)O in the sample was also calculated:

\[
n_{\text{D2O}} = \frac{m_{\text{D2O}} - (n_{\text{HOD}} \cdot M_{\text{HOD}})}{M_{\text{D2O}}},
\]

(2.2)

where \( m_{\text{D2O}} \) was the mass of D\(_2\)O (weighed to a relative precision \( \pm 0.02 \% \)) and \( M_{\text{HOD}} \) and \( M_{\text{D2O}} \) were the molar masses of HOD and D\(_2\)O, respectively. The mol ratio of \( n_{\text{HOD}} \) to the total moles of solvent, \( n_w \), was calculated from the following expression:

\[
\frac{n_{\text{HOD}}}{n_w} = \frac{n_{\text{HOD}}}{n_{\text{HOD}} + n_{\text{D2O}}},
\]

(2.3)

Appendix Table B.1 lists these CH\(_3\)COOD concentrations, their corresponding \( IP \) ratios of acetyl:methyl protons and the calculated isotopic purity of the D\(_2\)O:

\[
\frac{n_{\text{D2O}}}{n_w} = \frac{n_w - (1/2) \cdot n_{\text{H2O}}}{n_w}
\]

(2.4)

As shown in appendix Table B.1, the isotopic purity of the D\(_2\)O used in the studies presented in this thesis ranged from 99.695 % to 99.756 %, with an average of 99.730 %, and a standard deviation of 0.028 %. The acceptable purity of D\(_2\)O used in measurements has been reported at 99% (McDougall and Long, 1962; Arnett and McKelvey, 1969).
Midway through the project, after the work reported in Chapter 3 and before the work reported in Chapter 4, we purchased a Wissenschaftlich-Technische Werkstätten (WTW) model 3310 conductivity set meter, which attached to a Lr 325/01 pure water conductivity dip probe (with a measurement precision of ± 0.1%). To ensure that there was minimal external contamination of the D$_2$O that had been transferred to the 1 L HDPE bottles by any conducting species, we measured the conductivity, $\kappa$, of the D$_2$O, using the conductivity set meter and dip probe. Before use, the probe had been previously calibrated using a supplied, standard 5 $\mu$S·cm$^{-1}$ (± 2%) solution of KCl. Values of $\kappa$ for D$_2$O were measured under an Ar(g) atmosphere and were found to be no more than 0.5 $\mu$S·cm$^{-1}$ at 298.15 K, which was less than 1% of the conductivity of the solutions under investigation, thus we expect that the D$_2$O solvent had a minimal contribution to the solution conductivity.

2.2 High-Temperature High-Pressure Flow Conductivity Cell

2.2.1 Conductivity Cell and Assembly

The high-temperature high-pressure flow conductivity cell used to make the measurements in this thesis was originally designed at the University of Delaware by Zimmerman et al. (1993, 1995), and subsequently improved upon by Sharygin et al. (2002) and Hnedkovsky et al. (2005), so the cell could handle corrosive solutions. It is now known that flow systems are superior to static ones for the following reasons: (i) they can make high-accuracy measurements on dilute solutions, (ii) adsorption sites are saturated, (iii) impurities from the dissolution of cell components are swept away and (iv) the time for decomposition of the thermally sensitive samples is minimized (Tremaine et
al., 2004). A schematic of the conductivity cell is shown in Figure 2.2. The cell consists of a platinum/20% rhodium inlet tube (1.0 mm i.d., 1.6 mm o.d., 60 cm long) that leads into a platinized cell cavity, which serves as the outer electrode. A platinized inner electrode (1.6 mm o.d) is insulated from the outer electrode with a sapphire disk. After the solution passes through the cell, it travels through a tiny hole located at the end of the inner electrode, and then into a platinum exit tube which is connected to a condenser and back-pressure regulator. A diamond spacer is placed just beyond the electrodes in order to minimize any back flow of impurities. The cell body consists of three titanium cylindrical sections that are held securely in place with the use of screws and Belleville washers.

The cell was assembled in the machine shop at the University of Guelph by machinist Casey Gielen. The assembly procedure is shown in Figure 2.3 below. The titanium section of the cell, already attached to the platinum/20% rhodium inlet tube, was secured vertically by a series of support clamps, with the inlet tube pointing toward the ground. The gold washers were annealed, red-hot, prior to assembly using a blow-torch, in order to soften the metal. After cooling, one gold washer was placed directly on top of the first titanium section of the cell. The sapphire window was placed on top of the annealed gold washer, followed by another annealed gold washer. The inner electrode, attached to the platinum/20% rhodium outlet tube, was then placed on top of the second annealed gold washer, and was supported by clamps to keep it upright and properly aligned. The first ceramic insulator was placed on top of the inner electrode. The second ceramic insulator (which surrounds the annealed gold washers, sapphire disk, inner electrode, first ceramic spacer and rounded washers) was then carefully put into place,
Figure 2.2 A schematic of the high-temperature high-pressure conductivity flow cell. 1, Titanium sections of the cell; 2, Inlet tube (platinum/20% rhodium); 3, Cell cavity; 4, Outer electrode (lined with Platinum); 5, Inner electrode (lined with Platinum); 6, Diamond spacer; 7, Annealed gold washers; 8, Sapphire disk; 9, Rounded washers; 10, Ceramic insulators; 11, Screws; 12, Belleville washers; 13, Outlet tube (platinum/20% rhodium).
Figure 2.3 A schematic of the sequence of steps of assembly of the high-temperature high-pressure conductivity flow cell. The following is the order of assembly: 1, First titanium section of the cell; 2, Platinum inlet tube (platinum/20% rhodium); 3, First annealed gold washer; 4, Sapphire disk; 5, Second annealed gold washer; 6, Platinum outlet tube (platinum/20% rhodium); 7, First ceramic insulator; 8, Second ceramic insulator; 9, Rounded washers; 10, Second titanium section of the cell; 11, Third titanium section of the cell (plunger); 12, Screws; 13, Belleville washers.
making sure the annealed gold washers, sapphire disk, inner electrode and first ceramic spacer were all correctly positioned. The rounded washers were then added. The second titanium portion of the cell was put into place, making sure that all of the components were properly aligned. Finally, the third titanium portion of the cell, the plunger, was put into place. The first and second titanium portions of the cell were secured together using the screws. Each screw was tightened slightly, one at a time, then re-tightened (at least four times) in order to make sure the cell would not leak. The second and third titanium portions of the cell were also secured together, using screws and Belleville washers. The Belleville washers were placed between head of the screws and the third portion titanium portion of the cell, pushing against the screw heads and titanium cell assembly, ensuring that the cell was tight. Each screw was tightened slightly, one at a time, then re-tightened (at least four times) in order to make sure the entire cell assembly was secure. The cell was allowed to thermally equilibrate at the temperature of interest for at least 12 hours before use, in order to make sure that no leaks developed upon heating. This assembly procedure allowed the cell to reach the temperature and pressure conditions reported in this thesis ($T = 573.15$ K, $p = 20$ MPa).

### 2.2.2 Platinizing the Electrodes

Before the assembly described above, both the inner and outer electrodes in Figure 2.2 were plated with a thin layer of platinum black using the procedure reported by Ives and Janz (1961), which was also used by Madekufamba (2010). Both electrodes were cleaned using a 2.0 mol·L$^{-1}$ solution of H$_2$SO$_4$, prepared from ACS reagent-grade H$_2$SO$_4$ (Sigma-Aldrich, ACS reagent, 95-98%, # 32501). To clean the inner electrode,
the set-up shown in Figure 2.4a was used. A thin 99.9% platinum wire (Sigma-Aldrich, 99.9%, 0.25 mm diameter, 25 cm long, # 349402) was wound around a pencil to create a helix. The thin wire was then thoroughly rinsed with de-ionized water (18.2 MΩ·cm resistivity) and was immersed in some of the 2.0 mol·L⁻¹ solution of H₂SO₄. The inner electrode was placed carefully inside of the platinum wire helix and supported with a ring stand to make sure the inner electrode did not touch the thin platinum wire. The inner electrode was set-up as the anode and the helix was the cathode, connected to a Princeton Applied Research 363 potentiostat, donated to us by Dr. Grzegorz Szymanski. Using this procedure, the inner electrode was anodically cleaned by applying a current of 2 mA for 2 minutes, evolving H₂(g). To clean the outer electrode, the set-up shown in Figure 2.4b was used. A platinum rod (Sigma-Aldrich, 99.9%, 1.00 mm diameter, 3.25 cm long, # 327492) was carefully placed inside the area designated as the cell cavity in Figure 2.2, ensuring that the platinum rod did not touch the outer electrode. Enough 2.0 mol·L⁻¹ H₂SO₄ was injected into the platinum inlet tube, directly attached to the outer electrode (shown in Figures 2.2 and 2.3), to fully fill the cell cavity. The platinum rod was used as the cathode and the outer electrode as the anode, attached to the potentiostat. The outer electrode was cleaned by applying a current of 6 mA for 6 minutes, evolving H₂(g). After the cleaning, each electrode was thoroughly rinsed with de-ionized water (18.2 MΩ·cm resistivity).

Each electrode was then re-platinized using a solution of H₂PtCl₆ in HCl. A solution of H₂PtCl₆ (Sigma-Aldrich, 8 wt %, # 262587) was diluted with HCl (Sigma-Aldrich, 37%, # 320331) and de-ionized H₂O to create a solution of platinum black (2 wt% H₂PtCl₆ in 2 mol·L⁻¹ HCl). Using the set-up in Figure 2.4a, the inner electrode and
Figure 2.4  Schematic of the procedure used to platinize the electrodes of the high-temperature high-pressure conductivity flow cell.  a) Set-up for cleaning and platinizing the inner electrode; b) Set-up for cleaning and platinizing the outer electrode.  1, \( \text{H}_2\text{SO}_4 \) or platinum black solution; 2, Leads connecting the platinum electrodes or wires to the potentiostat; 3, Princeton Applied Research 363 potentiostat; 4, Ring stand; 5, Inner electrode; 6, Platinum wire; 7, Outer electrode; 8, Platinum rod.
platinum wire were now immersed in the platinum black solution. The polarity on the potentiostat was reversed, causing the inner electrode to become the cathode and the platinum wire to become the anode. The inner electrode was cathodically platinized by applying a current of 2 mA for 2 minutes. Using the set-up in Figure 2.4b, platinum black solution was injected up the platinum inlet tube, filling the cell cavity. The outer electrode was now used as the cathode and the platinum rod was used as the anode. The outer electrode was cathodically platinized by applying a current of 6 mA for 6 minutes. Both electrodes were rinsed thoroughly with de-ionized water before the cell was assembled.

2.2.3 Flow-Injection System

Figure 2.5 below shows a schematic of the high-temperature high-pressure flow system for the conductivity cell. This is a modification of the system reported by Méndez De Leo and Wood (2005). The solutions were injected into the high-temperature high-pressure AC conductivity flow cell (described in detail below) using peristaltic and high-precision liquid chromatography (HPLC) pumps, under an overpressure of Ar(g), to ensure that the solutions were not exposed to the atmosphere before the conductivity measurements were made. Solution pressure was regulated using a Circle Seal Controls Inc. model BPR21U25512 6000 psi (40 MPa) back pressure regulator charged at the required constant pressure from a high-pressure N\textsubscript{2}(g) tank. Pressure was monitored with a Paroscientific Inc. Digiquartz portable standard 760-6k pressure transducer. Pure, de-ionized reference water (18.2 MΩ·cm resistivity) was passed through the conductance cell (flow rate = 0.5 mL·min\textsuperscript{-1}) using a Lab Alliance series 1500 HPLC pump (HPLC
Figure 2.5  Schematic of the flow system for the high-temperature high-pressure conductivity cell. 1, Ar(g) tank; 2, 250 mL Pyrex© bottles containing solution of interest; 3, 14-port actuator; 4, Peristaltic pump; 5, Reference 18.2 MΩ·cm H₂O; 6, HPLC pumps; 7, Pressure transducer; 8, 6-port injection valves, attached to 2-position electronic actuators; 9, Waste beaker; 10, Delay loop; 11, Check valve; 12, Conductivity cell shown in Figure 2.1; 13, Whitey 6000 psi Check valve; 14, N₂(g) tank; 15, Back pressure regulator; 16, Waste beaker; 17, Insulated box; 18, Main heater; 19, Resistance temperature detector (RTD); 20, Proportional-integral-derivative (PID) controller; 21, Cell heaters (x 2); 22, RTD; 23, PID controller; 24, Platinum resistance thermometer (PRT); 25, PRT interface to computer; 26, Thermocouples; 27, PID controller; 28, Pre-heater coil around inlet tube; 29, RCL meter; 30, Personal computer (PC).
pump 1, shown in Figure 2.6 below). As shown in Figure 2.6a, when both 6-port injection valves (each attached to a VICI 2-position electronic actuator) were set to the “load” position, the reference water flowed through the conductance cell using HPLC pump 1, while a solution of interest was loaded into the delay loop using the Cheminert 08U-0560L 14-port actuator, connected to a Cole-Parmer Masterflex Easyload II 77201-60 peristaltic pump (this was defined as the “Load” setting on the flow system). When the peristaltic pump turned off, injection valve 1 was switched to the “inject” position (Figure 2.6b). HPLC pump 2 was then turned on and the reservoir water was pumped into the sample loop to pressurize the solution at the value set by the back-pressure regulator (this was defined as the “Pressurize” setting on the flow system). Once the solution in the sample loop was pressurized, HPLC pump 2 was turned off; injection valve 2 was switched to the “Inject” position (Figure 2.6c) and the solution was then injected into the conductivity cell at a flow rate = 0.5 mL·min⁻¹ (this was defined as the “Inject” setting on the flow system). Reservoir water then followed the solution, maintaining a constant flow rate of 0.5 mL·min⁻¹. After flowing through the conductivity cell, the solution and reservoir water passed through additional tubing, allowing the solution to cool. Finally, the solution and reservoir water flowed through the back pressure regulator, then into the waste beaker for disposal. Using this technique, reservoir water, solution and reservoir water were injected sequentially, maintaining pressure and minimizing any systematic errors that could arise from cooling and re-heating the conductance cell.
Figure 2.6  Schematic of the flow system for the high-temperature high-pressure conductivity cell. 1, Reference 18.2 MΩ•cm H₂O; 2, HPLC pump “1”; 3, HPLC pump “2”; 4, Pressure transducer; 5, Injection valve 1; 6, Injection valve 2; 7, Delay loop. a) “Load” setting, both injection valves are set to the “Load” position; b) “Pressurize” setting, injection valve 1 is switched to the “Inject” position, injection valve 2 is kept in the “Load” position; c) “Inject” setting, both injection valves are in “Inject” position.
2.2.4 Temperature Control

In order to control the temperature of the cell, three heating systems were used, as shown in Figure 2.5 above (Zimmerman et al., 2012a, 2012b). A main heater within a large insulated box heated the cell, and surrounding area, to a temperature approximately 5 K below that of the conductivity cell. A Pt 1000 Ω resistance temperature detector (RTD) measured the temperature of the insulated box and an Omega CNi3254 proportional-integral-derivative (PID) controller was used to maintain the temperature of the air surrounding the cell in the box to a relative precision of ± 1 K. Two additional cell heaters, placed within drilled holes in the titanium block of the cell, heated the conductivity cell to the temperature of interest. Another Pt 1000 Ω RTD, placed within a drilled hole in the titanium block of the cell, was used to measure the temperature of the cell, and a Leeds & Northrup 6430 Series Electromax III PID controller was used to control the temperature of the cell to ± 0.01 K. A platinum resistance thermometer, consisting of a Hart Scientific 5612 probe and 5707 6 ½ digit DMM, also placed within a drilled hole in the titanium block of the cell, measured the cell temperature to ± 0.02 K. Solution entering the cell was heated along the platinum/20% rhodium inlet tube using a pre-heating system that consisted of a pre-heater coil, PID control feedback system and two thermocouples. One thermocouple was attached to the base of the inlet tube connected to the titanium cell and the other thermocouple was attached directly to the titanium cell body. This allowed the pre-heating system to measure the potential difference between the thermocouple attached to the inlet tube and the thermocouple attached to the cell itself, which was directly proportional to the temperature difference between the titanium cell and the solution as it entered the cell. In response to the
potential difference between the thermocouples at the inlet tube and the titanium cell, an Automation Direct Solo 4824 PID system applied heat to the pre-heater coil in order to keep the temperature of the solution to equal the temperature of the cell (Zimmermann et al., 2012a, 2012b). The total uncertainty in temperature was estimated to be ± 0.02 K (Madekufamba, 2010; Erickson et al., 2011).

### 2.2.5 Measurements of Solution Resistance and Conductivity

Measurements of solution impedance were made as a function of frequency using a four-wire measurement from a Fluke PM6304 Programmable RCL meter. Two silver soldered leads were attached to the platinum/20% rhodium inlet and outlet tubes. The ground connections were made to the inlet and outlet tubing before and after the flow cell. Resulting voltage drops across the two electrodes were used to calculate the solution resistance, $R_s$, using equation (1.55). Real and imaginary components of the solution resistance were measured at frequencies of 100, 200, 500, 1000, 2000, 3000, 5000, 8000, and 10000 Hz. Recordings of real and imaginary impedances at each of these frequencies, as well as temperature (°C) and pressure (psi), were recorded on a personal computer as a function of time using a LabView® program, written at the University of Delaware by Dr. Lucila Méndez De Leo.

To obtain values of $R_s$ from the impedance measurements, both the Nyquist plot technique (described in Section 1.6.2) and the Hnedkovsky method (described in Section 1.6.3) were used. Initially, the Nyquist plot technique was used to determine values of $R_s$ for KCl, since this technique was also used for the measurements on acetic acid systems (which will be discussed in Chapter 3). To calculate values of $R_s$ for the solvent using the
With assistance from Professor Gregory Zimmerman (Bloomsburg University), we found that the best way to extrapolate the semi-circle portion of Figure 1.14 to \( Z_{lm} = 0 \) was to fix two of the four parameters that were considered at high values of frequency, \( \omega \): \( C_{cell}, R_{ct}, C_D \) and \( R_s \). Due to their minimal effect on the impedance, \( R_{ct} \) and \( C_D \) were initially fixed to very small values. Eventually, through multiple trials, it was decided that the values of \( R_{ct} \) and \( C_D \) be fixed to zero and 100 pF, respectively. \( C_{cell} \) and \( R_s \) were then used as adjustable parameters. To calculate values of \( R_s \) for solutions, the values of \( C_{cell}, R_{ct} \) and \( C_D \) were fixed to the same values reported for the solvent. \( R_s, \alpha_W \) and \( C_I \) were set to be adjustable parameters. Values for \( \alpha_W \) and \( C_I \) were calculated from an extrapolation of the Warburg line to \( Z_{lm} = 0 \) (see Figure 1.15), and used to calculate the value of \( R_s \). In our second set of experimental measurements on phosphoric acid (which will be discussed in Chapter 4), the Hnedkovsky method (Hnedkovsky et al., 2005) was used to determine values of \( R_s \) for KCl. To calculate numerical values for the adjustable parameters in the equivalent circuit and the Hnedkovsky extrapolation techniques, initial values for each of the parameters were assigned. Then, we performed a non-linear least-squares regression using the Levenberg-Marquardt fitting algorithm within our Wolfram Mathematica\textsuperscript{®} software (Press et al., 1992; Wolfram, 2003). The iteration cycle was continued until the fit converged to within the default tolerance of ± 0.0001.

Experimental values of conductivity, \( \kappa_{expt} \), were calculated from values of \( R_s \) and \( k_{cell} \) using equation (1.56). Values of \( \kappa_{expt} \) for neutral salt solutions were corrected, by
removing contributions from the solvent, using the equations reported by Sharygin et al. (2002) and Zimmerman and Wood (2002):

\[ \kappa_{\text{corr}} = \kappa_{\text{expt}} - (\kappa_{w}^{\text{expt}}), \]  

(2.5)

where \( \kappa_{w}^{\text{expt}} \) is the experimentally measured conductivity of the solvent. Acids and bases, or their conjugates, shift the auto-ionization equilibrium state of the solvent in solution towards the neutral solvent, decreasing the number of \( \text{H}^+ \) and \( \text{OH}^- \) ions from the solvent and lowering the solvent’s contribution to the solution conductivity. Following Sharygin et al. (2002), for the solutions of acetic and phosphoric acid, as well as their conjugate bases, acetate and dihydrogen phosphate: \( \kappa_w \), the conductivity of the pure solvent, was subtracted from \( \kappa_{w}^{\text{expt}} \) in equation (2.5):

\[ \kappa_{\text{corr}} = \kappa_{\text{expt}} - (\kappa_{w}^{\text{expt}} - \kappa_w) \]  

(2.6)

Values of \( \kappa_w \) for \( \text{H}_2\text{O} \) were calculated as follows:

\[ \kappa_w = (\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}) \cdot (K_{w,\text{H}_2\text{O}})^{1/2} \cdot \rho_{\text{H}_2\text{O}}, \]  

(2.7)

where values of \( \lambda^\circ \) for \( \text{H}^+ \) and \( \text{OH}^- \) were calculated from a relationship that relates ionic conductance to solvent density from Marshall (1987b) and values of \( K_{w,\text{H}_2\text{O}} \) were obtained from the equation of state reported by Marshall and Franck (1981). Values of \( \kappa_w \) for \( \text{D}_2\text{O} \) were calculated in a similar manner, where values of \( K_{w,\text{D}_2\text{O}} \) for \( \text{D}_2\text{O} \) from Mesmer and Herting (1978) were used. To date, the only reported values of ionic molar conductivity for \( \text{D}^+ \) and \( \text{OD}^- \) were obtained at temperatures below 338.15 K (Tada et al., 1992). Therefore, to estimate values of \( \lambda^\circ \) for \( \text{D}^+ \) and \( \text{OD}^- \) at the temperature conditions in this study, values of \( \lambda^\circ \) for \( \text{H}^+ \) and \( \text{OH}^- \) from Marshall (1987b) were used, but corrected for the difference in solvent density.
2.2.6 Calculation of the Cell Constant

In order to calculate the value of \(k_{\text{cell}}\) (\(k_{\text{cell}} = d/A\), described in Section 1.6.1), conductivity measurements on well-studied systems need to be made, and then compared to accurate literature results. We have adopted the procedure used by Zimmerman et al. (2002, 2007, 2009) to calculate values of \(k_{\text{cell}}\), which is based on the accurate values of \(\kappa\) for aqueous solutions of KCl, reported by Benson and Gordon (1945) and Barthel et al. (1980). A stock solution of \(m = 0.3207\) mol·kg\(^{-1}\) KCl (Alfa Aesar, 99.995%, metals basis, #87626) was prepared, by mass, to a relative precision of \(\pm 2\cdot10^{-5}\) %, using pure, deionized \(\text{H}_2\text{O}\) (18.2 MΩ·cm resistivity). As an example from which more dilute solutions were made, five solutions of KCl over the molality range \(m = 1.688\cdot10^{-4}\) to \(m = 9.537\cdot10^{-3}\) mol·kg\(^{-1}\) were prepared from this stock solution by mass using the pure, deionized water. The solution resistance of each of these solutions was measured in the AC conductivity flow cell at 298.15 K and 18.62 MPa. Values of \(k_{\text{cell}}\) were calculated using values of \(\kappa\) for KCl, measured on our cell, and comparing these values with Barthel’s (1980) values of \(\kappa\) for KCl. Each of these measurements was made five times, and then averaged. Appendix Table B.2 shows this sample set of experimental data used to calculate \(k_{\text{cell}}\), which, in that sample set, resulted in an average value of \(k_{\text{cell}} = (0.06479 \pm 0.00027)\) cm\(^{-1}\).

Under hydrothermal conditions, temperature-induced expansion of the sapphire disk, diamond spacer and platinum can affect the distances between the inner and outer electrodes, and the surface area of the electrodes. Therefore, it is not a suitable approximation to assume that \(k_{\text{cell}}\) is temperature independent. Based on the derivation reported by Zimmermann (1993), high temperature values of \(k_{\text{cell}}\) are calculated from
room temperature values of $k_{\text{cell}}$ using the change in the surface area of the inner electrode. For the cylindrical design of our cell:

$$k_{\text{cell}} = \frac{1}{2 \cdot \pi \cdot L_1} \cdot \ln \left[ \frac{r_2}{r_1} \right],$$  

(2.8)

where $L_1$ is the length of the inner electrode, and $r_1$ and $r_2$ are the radii of the outer and inner electrodes, respectively. Since the outer and inner electrodes are made of the same material, their thermal expansions with respect to temperature cancel. Therefore, the relationship between $k_{\text{cell}}$ measured at room temperature ($k_{\text{cell}}$) and a calculated value of $k_{\text{cell}}$ at high temperature ($k_{\text{cell,highT}}$) is made by considering the change in $L_1$ as a function of temperature:

$$k_{\text{cell,highT}} = k_{\text{cell}} \cdot \left( \frac{L_1}{L_{1,\text{highT}}} \right),$$  

(2.9)

where $L_{1,\text{highT}}$ is the length of the inner electrode at high temperature. From the cell design in Figure 2.2, it becomes evident that only part of the inner electrode in contact with the solution is used to make the impedance measurements. Therefore the value of $L_1$ is calculated as follows:

$$L_1 = L_{\text{Pt}} - L_{\text{saph}} - L_{\text{diam}},$$  

(2.10)

where $L_{\text{Pt}}$ is the total length of the inner platinum electrode, $L_{\text{saph}}$ is the length of the sapphire disk and $L_{\text{diam}}$ is the length of the diamond spacer, all at room temperature. Equations for the change in length of platinum and sapphire have been given as a function of temperature by Touloukian et al. (1975a, 1975b):

$$L_{\text{Pt,highT}} - L_{\text{Pt}} = L_{\text{Pt}} \cdot \left[ 9.122 \cdot 10^{-4} \cdot (T - 293) + 7.467 \cdot 10^{-8} \cdot (T - 293)^2 ight. + \left. 4.258 \cdot 10^{-11} \cdot (T - 293)^3 \right]$$  

(2.11)
where \( t \) is the temperature in °C. Measurements of the thermal expansion of platinum reported by Touloukian \textit{et al.} (1975a) were made at 293 K. Therefore, the temperature of “293” reported in equation (2.11) is present in order to account for this. An equation for the expansion of diamond as a function of temperature was calculated using temperature-dependent expansion values reported by the Harris Diamond Corporation (1993):

\[
L_{\text{diam,highT}} - L_{\text{diam}} = L_{\text{diam}} \cdot \left[ -4.345 \cdot 10^{-7} \cdot T + 3.373 \cdot 10^{-9} \cdot T^2 + 2.792 \cdot 10^{-12} \cdot T^3 \right] \tag{2.13}
\]

Equations (2.9) to (2.13) yields the following expression for \( k_{\text{cell,highT}} \), relative to the values of \( k_{\text{cell}} \) at 298 K:

\[
k_{\text{cell,highT}} = k_{\text{cell}} \cdot \frac{L_{\text{Pt}} - L_{\text{saph}} - L_{\text{diam}}}{L_{\text{Pt,highT}} - L_{\text{saph,highT}} - L_{\text{diam,highT}}} \tag{2.14}
\]

Calculated values of \( k_{\text{cell,highT}} \) at temperatures as high as 571 K, reported in this thesis, were found to differ by no more than 1.0 %, when compared to those values of \( k_{\text{cell}} \) measured at 298.15 K.

2.3 Experimental Methodology

2.3.1 Calculation of \( pK_{\text{aq}} \) from Conductivity Measurements

When measuring the extent of a reaction for a weak electrolyte (reaction (1.54)), the value of \( K_a \) for a weak acid, HA, is related to the degree of ionization, \( \alpha \), as follows:

\[
K_a = \frac{\alpha^2 \cdot c \cdot \gamma_{\pm}^2}{(1 - \alpha)} \tag{2.15}
\]
where \( c \) is the concentration of the solution and \( \gamma_\pm \) is the mean activity coefficient of the ions in the solution, which is calculated using the model proposed by Debye and Hückel (equations (1.31) to (1.33)), and:

\[
\alpha = \frac{\Lambda^{\text{exp}}}{\lambda_{H^+} + \lambda_{A^-}} \tag{2.16}
\]

Here, \( \Lambda^{\text{exp}} \) (the experimental molar conductivity of the weak acid) and \( \lambda_{H^+} + \lambda_{A^-} \) (the individual ionic contributions to the molar conductivity of the dissociated acid) are at the same ionic strength, \( \alpha c \). At concentrations below \( c = 10^{-2} \text{ mol·L}^{-1} \), values of \( \lambda \) are additive quantities (MacInnes, 1938). Therefore, values of \( \lambda_{H^+} + \lambda_{A^-} \) can be obtained by calculating values of \( \Lambda \) at the same ionic strength for multiple strong electrolytes, and then summing them:

\[
\lambda_{H^+} + \lambda_{A^-} = \lambda_{H^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} + \lambda_{\text{Na}^+} + \lambda_{A^-} = \Lambda_{\text{HCl}} - \Lambda_{\text{NaCl}} + \Lambda_{\text{NaA}}, \tag{2.17}
\]

where NaA is the sodium salt of the weak acid.

To calculate values of \( \Lambda_{\text{HCl}}, \Lambda_{\text{NaCl}} \) and \( \Lambda_{\text{NaA}} \) at the same concentration, the FHFP (Fernández-Prini, 1973) equation (equation (1.71)) is used:

\[
\Lambda = \Lambda^o - S \cdot c^{1/2} + E \cdot c \cdot \ln[c] + J_1 \cdot c - J_2 \cdot c^{3/2} \tag{2.18}
\]

The FHFP equation is the preferred choice for modeling \( \Lambda \) as a function of \( c \) in this study, because it is relatively simple and is accurate under the conditions used in this study (Bianchi et al., 2000). As will be discussed in Chapters 3 and 4, concentration ranges for solutions used in our measurements do not exceed \( c = 0.01 \text{ mol·L}^{-1} \), and all solutions reported in this thesis contain only symmetrical electrolytes, consistent with the validity of the model at 298 K. The parameter, \( S \), presented in equation (2.18) is calculated from the transport, dielectric and thermodynamic properties of the solvent; which are well
known for H$_2$O and for D$_2$O (Hill et al., 1982; Kestin et al., 1984; Okada et al., 1999; Wagner and Pruß, 2002).

Figure 2.7a below shows a flow chart of the iterative cycle used to calculate values of $\Lambda^\circ$ from experimental values of $\Lambda$ for HCl, NaA and NaCl, which are dilute strong electrolytes (all at approximately the same concentration, $c$). A trial value of $\Lambda^\circ$, $\Lambda_{\text{trial}}^\circ$, is initially set for the parameters $E, J_1, J_2$ and $\Delta\delta$ (see equations (1.72) to (1.83)), and a value of $\Lambda^\circ$, $\Lambda_{\text{calc.}}^\circ$, is then calculated for the strong electrolyte at concentration, $c$, using equation (2.18). $\Lambda_{\text{calc.}}^\circ$ is then compared to $\Lambda_{\text{trial}}^\circ$, to see if the relative difference between the two is less than 1·10$^{-8}$ (this was an arbitrary value that set to make sure that the iteration cycle was thorough). If the relative difference between the trial and calculated values of $\Lambda^\circ$ is greater than 1·10$^{-8}$, then the value of $\Lambda_{\text{calc.}}^\circ$ now becomes $\Lambda_{\text{trial}}^\circ$, and is used to re-calculate a new value of $\Lambda_{\text{calc.}}^\circ$. This iteration cycle is repeated until $\Lambda_{\text{trial}}^\circ$ and $\Lambda_{\text{calc.}}^\circ$ have a relative difference of no more than 1·10$^{-8}$. Once a value of $\Lambda^\circ$ is successfully calculated, a value of $\Lambda$ at any concentration can be calculated from equation (2.18).

The value of $\Lambda^\circ$ for the fully dissociated acid is represented as the sum of values of $\Lambda^\circ$ for each of the strong electrolytes:

$$\Lambda_{\text{HA}}^\circ = \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ + \Lambda_{\text{NaA}}^\circ = \Lambda_{\text{H}^+}^\circ + \Lambda_{\text{A}^-}^\circ \quad (2.19)$$

Once $\Lambda_{\text{HA}}^\circ$ has been determined, values of $\lambda_{\text{H}^+} + \lambda_{\text{A}^-}$ at the same ionic strength, $\alpha \cdot c$, can be represented as a function of ionic strength using a modified version of equation (1.71):

$$\lambda_{\text{H}^+} + \lambda_{\text{A}^-} = \Lambda^\circ - S \cdot (\alpha \cdot c)^{1/2} + E \cdot (\alpha \cdot c) \cdot \ln[\alpha \cdot c] + J_1 \cdot (\alpha \cdot c) - J_2 \cdot (\alpha \cdot c)^{3/2} \quad (2.20)$$

If equations (2.16) and (2.20) are combined, the following equation (equation (1.85)) is obtained:
Calculate value of Λ° (equation (2.18))

While 
\[ \frac{\Lambda_{\text{calc.}} - \Lambda_{\text{trial}}}{\Lambda_{\text{trial}}} > 10^{-8} \]

\[ \Lambda° \]

Trial estimation of Λ°

Trial estimations of \( \alpha \) and \( [\lambda_H+ + \lambda_{A^-}] \)

Calculate value of \( [\lambda_H+ + \lambda_{A^-}]_{\text{calc.}} \) (equation (2.19))

While 
\[ \frac{\alpha_{\text{calc.}} - \alpha_{\text{trial}}}{\alpha_{\text{trial}}} > 10^{-8} \]

Calculate value of \( \alpha_{\text{est.}} \) (equation (2.16))

\[ \alpha \]

Calculate value of \( K_a \) (equation (2.15))

**Figure 2.7** Flow chart for the process used to calculate values of \( K_a \) using the FHFP equation. a) Calculation of values of \( \Lambda° \) for strong electrolytes; b) Calculation of values of \( \alpha \) and \( [\lambda_H+ + \lambda_{A^-}] \) for weak acids, used to calculate values of \( K_a \).
\[ \Lambda^\text{exp} = \alpha \left[ \Lambda^0 - S \cdot (\alpha \cdot c)^{1/2} + E \cdot (\alpha \cdot c) \cdot \ln(\alpha \cdot c) + J_1 \cdot (\alpha \cdot c) - J_2 \cdot (\alpha \cdot c)^{3/2} \right] \] (2.21)

\( \Lambda^\text{exp} \) is the experimental molar conductivity of the partially dissociated acid. The degree of dissociation, \( \alpha \), is calculated iteratively, as follows: Trial values of \( \alpha \) and \( \lambda_{H^+} + \lambda_{A^-} \) are initially used. The trial value of \( \alpha \), \( \alpha_{\text{trial}} \), is placed into equation (2.20) to calculate an estimated value of \( \lambda_{H^+} + \lambda_{A^-} \) (\( [\lambda_{H^+} + \lambda_{A^-}]_{\text{calc.}} \)) and the trial value of \( \lambda_{H^+} + \lambda_{A^-} \) is placed into equation (2.16) to calculate an estimated value of \( \alpha \) (\( \alpha_{\text{calc.}} \)). \( \alpha_{\text{trial}} \) is then compared to \( \alpha_{\text{calc.}} \) in order to see if relative difference between the two is less than 1\( \cdot \)10\(^{-8} \) (this was an arbitrary value that set to make sure that the iteration cycle was thorough). If the relative difference between \( \alpha_{\text{trial}} \) and \( \alpha_{\text{calc.}} \) is greater than 1\( \cdot \)10\(^{-8} \), then two calculations are performed. First, \( \alpha_{\text{calc.}} \) becomes \( \alpha_{\text{trial}} \), and is placed into equation (2.20) to calculate a new value of \( [\lambda_{H^+} + \lambda_{A^-}]_{\text{calc.}} \). Second, the value of \( [\lambda_{H^+} + \lambda_{A^-}]_{\text{calc.}} \) is placed into equation (2.16) to calculate another new value of \( \alpha_{\text{calc.}} \). This iteration cycle is repeated until the values of \( \alpha_{\text{trial}} \) and \( \alpha_{\text{calc.}} \) have a relative difference of no more than 1\( \cdot \)10\(^{-8} \). Once a value of \( \alpha \) is calculated, a value of \( K_a \) for the weak acid is then be calculated using equation (2.15). A flow-chart depicting this calculation cycle is shown in Figure 2.7b.

Solution molalities were converted to molarities using equations (1.88) and (1.89). Values of \( \rho_w \) for H\(_2\)O have been calculated by Wagner and Pruß (2002) and values of \( \rho_w \) for D\(_2\)O have been calculated by an equation of state from Hill (Hill et al., 1982; Kestin and Sengers, 1986). For strong electrolytes in solution, values of \( V^\circ \) are calculated from the HKF equation within SUPCRT (Johnson et al., 1992). For weak acids, values of \( V^\circ \) need to be calculated using values of \( \alpha \):

\[ V^\circ = \alpha \cdot V_{A^-}^\circ + \alpha \cdot V_{H^+}^\circ + (1 - \alpha) \cdot V_{HA}^\circ, \] (2.22)
where $V_{H^+}^\circ$ is taken to be zero. For dilute solutions ($m < 0.02 \text{ mol}\cdot\text{kg}^{-1}$) at temperatures below the critical point, differences between the values of $\rho$ and $\rho_{H2O}$ are usually negligible. Therefore, values of $\rho$ are usually taken to be approximately equal to $\rho_{H2O}$ (Gruszkiwicz and Wood, 1997). In this study, we have chosen to initially assume that the values of $\rho$ for the weak acid and $\rho_w$ are the same, in order to estimate values of $\alpha$ for the weak acid in H$_2$O and D$_2$O, which are then used to calculate values of $V^\circ$, using equation (2.22). Using these calculated values of $V^\circ$, actual values of $c$ for the weak acid in each solvent are then calculated.

### 2.3.2 Experimental Design

The solvents and solutions in H$_2$O and D$_2$O were injected into the flow conductivity cell in the following order: H$_2$O, D$_2$O, NaCl (in H$_2$O), NaCl (in D$_2$O), HA, DA, NaA (in H$_2$O), NaA (in D$_2$O), HCl, DCl, NaOH, NaOD, H$_2$O and D$_2$O, as shown in Figure 2.8 below. The injections were done in sequence: first a solution in H$_2$O and then a corresponding solution in D$_2$O, at the same temperature, pressure and flow rate, with reservoir water flowing after each solution (to clean the cell). This sequence was repeated for each set of electrolyte or acid solution in H$_2$O and D$_2$O. The sequential injection of solutions eliminated the needed to re-set the temperature and pressure conditions on the cell, thus removing any systematic error associated with making the impedance measurements. It took approximately 1.5 hours to make the impedance measurements on each solvent or solution, followed by approximately 2 hours to clean out the cell with H$_2$O from the reservoir. A total set of experimental measurements at each temperature took approximately 50 hours to complete.
Figure 2.8  Sequence of chemical injections into high temperature high-pressure AC conductance cell in order to calculate values of $pK_a$ for the weak acids HA and DA. The y-axis shows relative values of $\kappa$ for each solution at an approximate ionic strength, $I = 10^{-3}$ mol·kg$^{-1}$. 
PART II:

HIGH TEMPERATURE HIGH PRESSURE DEUTERIUM ISOTOPE EFFECT
STUDIES ON WEAK ACID SYSTEMS
CHAPTER 3
DEUTERIUM ISOTOPE EFFECTS ON THE IONIZATION OF AQUEOUS ACETIC ACID FROM 368 K TO 548 K

3.1 Introduction

Measurements of the ionization constants for acetic acid in light and heavy water, \(K_{\text{HAc}}\) and \(K_{\text{DAc}}\), have been made from 368 to 548 K at \(p = 20\) MPa using a state-of-the-art, high-temperature, high-pressure flow AC conductivity cell described in Chapter 2. The instrument is capable of operating up to and beyond the critical point of water, at ionic strengths as low as \(I = 10^{-5}\) mol·kg\(^{-1}\). The measurements followed the experimental design discussed in Section 2.3.2, in which solutions of sodium chloride, acetic acid, sodium acetate and hydrochloric acid, in both H\(_2\)O and D\(_2\)O, were injected in sequence at fixed temperature and pressure. This procedure causes systematic errors in the experimental molar conductivities of solutions in the two solvents to cancel out, thus yielding more precise values of the deuterium isotope effect, \(\Delta pK_{\text{aq}}\).

Results and interpretations presented in this chapter have been previously reported in the literature by Erickson et al. (2011). However, after publication, errors were found within the Mathematica® subroutines I had designed for calculating the values of \(\Delta pK_{\text{aq}}\). A detailed account of these errors and subsequent corrections is given Appendix C, Part I.

3.2 Experimental

3.2.1 Solution Preparation

The stock solutions were prepared in H\(_2\)O and D\(_2\)O as follows: 1.0 mol·kg\(^{-1}\) solutions of CH\(_3\)COOH (Sigma Aldrich, #537020, 99.85%) and CH\(_3\)COOD (Sigma
Aldrich, #151777, 99 atom % D) were prepared from glacial stock solutions, without further purification. Stock solutions of HCl (Sigma Aldrich, #318965, 0.1 N standard), DCl (Sigma Aldrich, #543047, 35 wt % in D₂O, 99 atom % D), NaOH (Sigma Aldrich, #319511, 1.0 N standard) and NaOD (Sigma Aldrich, #372072, 40 wt % in D₂O, 99.5 atom % D) were prepared by dilution to approximately 0.1 mol·kg⁻¹. The HCl and DCl solutions were standardized by titration against a standard NaOH solution, at 298.15 K, and were found to have molalities of \( m = (0.1299 \pm 0.0003) \text{ mol·kg}^{-1} \) for HCl and \( m = (0.4677 \pm 0.0013) \text{ mol·kg}^{-1} \) for DCl. The NaOH and NaOD solutions were standardized by titration against a standard HCl solution, also at 298.15 K, and were found to have molalities of \( m = (0.1047 \pm 0.0014) \text{ mol·kg}^{-1} \) for NaOH and \( m = (0.2907 \pm 0.0022) \text{ mol·kg}^{-1} \) for NaOD. Stock solutions of \( m = 0.1112 \text{ mol·kg}^{-1} \) NaCl (Fisher Scientific, 99.99%) in H₂O, \( m = 0.07037 \text{ mol·kg}^{-1} \) NaCl (Fisher Scientific, 99.99%) in D₂O, \( m = 0.08494 \text{ mol·kg}^{-1} \) NaCH₃COO (Fisher Scientific, 99.4%) in H₂O and \( m = 0.09156 \text{ mol·kg}^{-1} \) NaCH₃COO (Fisher Scientific, 99.4%) in D₂O were prepared by mass from their salts. Each salt was dried at 423.15 K for 7 days, to constant mass, before use and weighed to a relative precision of ± 0.01 %. Pure, de-ionized H₂O (resistivity 18.2 MΩ·cm) was used in the preparation of the stock solutions in H₂O. D₂O (donated from Bruce Power, determined to be 99.730 mol % isotopically pure, see Section 2.1.3) was used in the preparation of the stock solutions in D₂O.

Subsequent solutions of CH₃COONa, HCl, NaCl and NaOH, all in H₂O, with an approximate molality \( m = 10^{-3} \text{ mol·kg}^{-1} \) in 18.2 MΩ·cm H₂O, were prepared by mass, to a relative precision of ± 0.2 %, by diluting the 0.1 mol·kg⁻¹ stock solutions. Care was taken to prevent any CO₂(g) contamination within the solutions by keeping a positive Ar(g)
pressure within sample bottles, since this could cause an unwanted formation of H$_2$CO$_3$(aq). Solutions of CH$_3$COONa, DCl, NaCl and NaOD, all in D$_2$O, all with the same approximate molality, $m = 10^{-3}$ mol·kg$^{-1}$, were prepared by mass, to a relative precision of ± 0.2 %, by diluting 0.1 mol·kg$^{-1}$ stock solutions with D$_2$O (99.730 mol % isotoically pure). The dilution process was done under an inert Ar(g) atmosphere in order to prevent any CO$_2$(g) or H contamination. Solutions of approximate molality $m = 10^{-3}$ mol·kg$^{-1}$ of CH$_3$COOH in 18.2 MΩ·cm H$_2$O and CH$_3$COOD in D$_2$O (99.730 mol % isotoically pure) under Ar(g) were also prepared by mass, to a relative precision of ± 0.2 %, by diluting the 1.0 mol·kg$^{-1}$ stock solutions with the appropriate solvents.

### 3.2.2 AC Conductivity Measurements

AC impedance data were collected for the full series of solutions: H$_2$O, D$_2$O, NaCl (in H$_2$O), NaCl (in D$_2$O), HAc, DAc, NaAc (in H$_2$O), NaAc (D$_2$O), HCl, DCl, NaOH, NaOD, D$_2$O and H$_2$O. Each solution was injected using the procedure described in Section 2.2.3. A schematic of the injection sequence was shown in Figure 2.8. The result of these measurements was a series of values for the real and imaginary impedance, equation (1.58):

$$Z = Z_{Re} - j \cdot Z_{Im},$$  \hspace{1cm} (3.1)

at frequencies of 100, 300, 500, 1000, 2000, 3000, 5000, 8000, and 10000 Hz. Values of solution resistance, $R_s$, for the solvents and each solution of interest were obtained by extrapolation of the impedance data collected, using the equivalent circuit extrapolation technique, described in Section 2.2.5. Numerical values for the adjustable parameters in the equivalent circuit were determined through non-linear least-squares regression, using
the Levenberg-Marquardt fitting algorithm. These were calculated for each species in H$_2$O, which are reported in Appendix Table C.4, and for each species in D$_2$O, which are reported in Table C.5. Comparisons of experimental and predicted values of $Z_{Re}$ and $Z_{Im}$, as well as the extrapolated values of $R_s$, for each species in H$_2$O and D$_2$O, are shown in the form of Nyquist plots, in Appendix Figures C.1 to C.36.

### 3.3 Methodology

Acetic acid, a weak electrolyte, ionizes in aqueous solution according to a single-step process, reaction (1.54):

$$\text{HAc} \rightleftharpoons \text{H}^+ + \text{Ac}^-$$

(1.54)

$$(1 - \alpha) \cdot c \quad \alpha \cdot c \quad \alpha \cdot c$$

(3.2)

where the degree of ionization, $\alpha$, in a solution of concentration, $c$, is used to determine the equilibrium constant that we seek to measure (equation (2.15)):

$$K_a = \frac{(\alpha)^2 \cdot c \cdot \gamma_{\pm}^2}{(1 - \alpha)}$$

(3.3)

Values of $c$ were calculated from the experimental molalities using equations (1.88) and (1.89):

$$c = \frac{m \cdot \rho \cdot w_1}{w_1 + w_2}$$

(3.4)

$$\rho = \frac{(M_2 \cdot \rho_w \cdot m) + (1000 \cdot \rho_w)}{(V^\circ \cdot \rho_w \cdot m) + 1000}$$

(3.5)

To calculate values of $V^\circ$ for the strong electrolytes: NaCl, CH$_3$COONa, HCl and NaOH, we summed values of $V^\circ$ for the corresponding ions, which were obtained from the SUPCRT program reported by Johnson et al. (1992). These values were assumed to be
the same for each species in H$_2$O and D$_2$O. For CH$_3$COOH, values of $V^\circ$ had to include the degree of dissociation, $\alpha$, equation (2.22):

$$V^\circ = \alpha \cdot V_{CH3COO^-}^\circ + \alpha \cdot V_{H^+}^\circ + (1 - \alpha) \cdot V_{CH3COOH}^\circ,$$

where $V^\circ$ for H$^+$ is taken to be zero. To do this, we began with the assumption of Gruszkiewicz and Wood (1997), that the value of $\rho$ for the weak acid and $\rho_w$ for the solvent are the same, in order to estimate a value of $\alpha$ for the weak acid in H$_2$O and D$_2$O. Then, using this estimated value of $\alpha$, the actual value of $c$ for acetic acid in each solvent was calculated using equations (3.4) and (3.5). Values of $\rho$ and $\rho_w$ are compared for each solution in H$_2$O and D$_2$O as a function of temperature in Appendix Tables C.6 and C.7, respectively, to prove that the two values differ only marginally, so that a second iteration was not necessary. Appendix Table C.8 reports values of $V^\circ$ for each species at our experimental conditions in H$_2$O (which are assumed to be the same in D$_2$O).

According to equations (2.16) and (2.17):

$$\alpha = \frac{\Lambda^{exp}}{\lambda_{H^+} + \lambda_{Ac^-}},$$

and:

$$\lambda_{H^+} + \lambda_{Ac^-} = \lambda_{H^+} + \lambda_{Cl^-} - \lambda_{Na^+} - \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{Ac^-} = \Lambda_{HCl} - \Lambda_{NaCl} + \Lambda_{NaAc},$$

so that values of $\alpha$ for HAc can be calculated from the experimental values of $\Lambda$ for HAc and experimental values of $\Lambda$ for HCl, NaCl and NaAc. It is known that HCl and NaCl are fully dissociated under our experimental conditions (Ho et al., 2000a, 2001). NaAc however, undergoes a modest degree of hydrolysis which requires a correction (to be discussed below).
To correct for small differences in the concentrations of solutions of NaCl, HCl and NaAc, we have made use of the FHFP model, equation (1.71):

\[
\Lambda = \Lambda^\circ - S \cdot c^{3/2} + E \cdot c \cdot \ln[c] + J_1 \cdot c - J_2 \cdot c^{3/2},
\]

(3.9)

to calculate values of \(\Lambda^\circ\) for HAc from values of \(\Lambda^\circ\) for NaCl, HCl and NaAc.

Values of \(K_a\) were calculated from equation (3.3), using values of \(\alpha\), which were calculated from the expression (equation (2.21)):

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

(3.10)

using the iterative process described in Section 2.3.1. The terms \(S, E, J_1\) and \(J_2\) are defined by equations (1.72) to (1.84). Equations (1.72) to (1.84) require known values of solvent density, viscosity and dielectric constant. Values of \(\rho_{H_2O}\) were obtained from Wagner and Pruß (2002) using the NIST software package entitled: “ASME and IAPWS Formulation for Water and Steam, Version 10.0”. Values of \(\rho_{D_2O}\) were obtained from Hill et al. (1982) and Kestin and Sengers (1986), using the NIST software package entitled: “REFPROP: Equations of State for Pure and Binary Fluids, Version 8.0”. Values of \(\eta_{H_2O}\) and \(\eta_{D_2O}\) were also obtained from the ASME IAPWS (version 10.0) and REFPROP (version 8.0) databases, respectively, which are based on the work of Wagner and Pruß (2002), Kestin et al. (1984) and the IAPWS formulation for water and steam (1994). Values of \(\varepsilon_{H_2O}\) were obtained from Fernández et al. (1997). Values of \(\varepsilon_{D_2O}\) were calculated using the method reported by Trevani et al. (2007), where values of \(\varepsilon_{H_2O}\) and \(\varepsilon_{D_2O}\) are assumed to be equal at the same number density at the same temperature. Values of \(\rho, \eta\) and \(\varepsilon\) for each solvent at each experimental temperature and pressure are reported in Part II of Appendix C, Table C.9.
3.4 Results

3.4.1 Values of $\Lambda$ and $\Lambda^o$

Corrected experimental values for the cell specific conductivity, $\kappa_{\text{corr}}$, of each solution, the corresponding molar conductivity, $\Lambda^{\text{exp}}$; and the cell constants, $k_{\text{cell}}$, are reported in Tables 3.1 and 3.2 below. At $T = 548.44$ K, DCI impedance data were collected separately due to a leak in the cell. Upon fixing the leak, a new value for $k_{\text{cell}}$ was measured and used. This is also reported in Table 3.2. The concentrations are tabulated in Tables 3.1 and 3.2 as both aquamolalities, $m_{\text{aq}} = (\text{mol solute})\cdot(55.509 \text{ mol solvent})^{-1}$, equation (1.90), and calculated molarities, $c = (\text{mol solute})\cdot(\text{L solution})^{-1}$, equation (3.4).

Values of the limiting conductance for each of the salt solutions, $\Lambda^o$, were calculated from the FHFP model, equation (3.9), using values for the distance of closest approach set equal to the Bjerrum distance, equation (1.84). The determination of $\lambda_{\text{Na}^+} + \lambda_{\text{Ac}^-}$ from $\Lambda_{\text{NaAc}}$ was complicated by the hydrolysis of the acetate anion, according to the reaction:

$$\text{HAc} + \text{OH}^- \rightleftharpoons \text{Ac}^- + \text{H}_2\text{O} \quad (3.11)$$

To address this concern, the degree of hydrolysis in light water was estimated from equilibrium constants for reaction (3.11), calculated from the HKF model reported by Shock and Helgeson (1990), using the SUPCRT92 software (Johnson et al., 1992). These agreed with calculations based on experimental values reported by Mesmer et al. (1989), to within a few percent. The degree of hydrolysis in D$_2$O was estimated by assuming that the equilibrium constant for reaction (3.11) was the same as that in H$_2$O, on an aquamolality scale. Calculated values of $\Lambda_{\text{NaOH}}^o$ and $\Lambda_{\text{NaOD}}^o$, reported in Tables 3.1 and
Table 3.1. Values of experimental molar conductivities, $\Lambda^\text{exp}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for NaCl(aq), HAc(aq), NaAc(aq), HCl(aq), and NaOH(aq) in H$_2$O from $T = 368$ K to $T = 548$ K at $p = 20$ MPa

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^\text{exp}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>106.96 ± 0.15</td>
<td>103.70 ± 0.15</td>
<td>35.416 ± 0.019</td>
<td>341.54 ± 0.51</td>
<td>344.39 ± 0.51</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>126.95 ± 0.13</td>
<td>123.08 ± 0.13</td>
<td>26.794 ± 0.011</td>
<td>217.70 ± 0.23</td>
<td>775.9 ± 11.5</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>80.51 ± 0.12</td>
<td>78.05 ± 0.12</td>
<td>21.4963 ± 0.0076</td>
<td>271.87 ± 0.38</td>
<td>274.15 ± 0.39</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>188.66 ± 0.57</td>
<td>182.90 ± 0.57</td>
<td>153.714 ± 0.062</td>
<td>840.4 ± 2.6</td>
<td>846.1 ± 2.6</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>164.9 ± 2.3</td>
<td>159.8 ± 2.3</td>
<td>90.885 ± 0.038</td>
<td>568.6 ± 8.2</td>
<td>572.9 ± 5.3</td>
</tr>
</tbody>
</table>

$T = (368.601 ± 0.045)$ K, $p = (17.5825 ± 0.0029)$ MPa

$k_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_{w}^\text{exp} = (1.4768 ± 0.0012) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^\text{exp}$</th>
<th>$\Lambda^\circ$</th>
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<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>106.96 ± 0.15</td>
<td>99.15 ± 0.15</td>
<td>52.030 ± 0.042</td>
<td>524.74 ± 0.84</td>
<td>529.56 ± 0.85</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>126.95 ± 0.13</td>
<td>117.69 ± 0.13</td>
<td>24.4988 ± 0.0086</td>
<td>208.17 ± 0.22</td>
<td>988.0 ± 14.1</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>80.51 ± 0.12</td>
<td>74.63 ± 0.12</td>
<td>32.9395 ± 0.0091</td>
<td>433.97 ± 0.60</td>
<td>437.77 ± 0.61</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>188.66 ± 0.57</td>
<td>174.89 ± 0.57</td>
<td>187.309 ± 0.097</td>
<td>1071.0 ± 3.3</td>
<td>1079.8 ± 3.3</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>164.9 ± 2.3</td>
<td>152.84 ± 2.3</td>
<td>115.282 ± 0.043</td>
<td>754.3 ± 10.3</td>
<td>761.2 ± 10.5</td>
</tr>
</tbody>
</table>

$T = (422.40 ± 0.10)$ K, $p = (17.5023 ± 0.0035)$ MPa

$k_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_{w}^\text{exp} = (2.7093 ± 0.0014) \cdot 10^{-6}$ S·cm$^{-1}$
Table 3.1.  Continued

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<tr>
<th>Solute</th>
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<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>193.74 ± 0.16</td>
<td>169.72 ± 0.16</td>
<td>113.64 ± 0.23</td>
<td>669.6 ± 1.5</td>
<td>679.3 ± 1.5</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>172.27 ± 0.13</td>
<td>150.91 ± 0.13</td>
<td>21.578 ± 0.027</td>
<td>142.99 ± 0.21</td>
<td>1170.1 ± 16.9</td>
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<tr>
<td>NaAc(aq)</td>
<td>64.78 ± 0.13</td>
<td>56.75 ± 0.13</td>
<td>34.199 ± 0.030</td>
<td>590.9 ± 1.2</td>
<td>595.6 ± 1.2</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>157.92 ± 0.50</td>
<td>138.34 ± 0.50</td>
<td>172.237 ± 0.069</td>
<td>1245.0 ± 4.0</td>
<td>1253.8 ± 4.0</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>130.1 ± 1.8</td>
<td>114.0 ± 1.8</td>
<td>108.733 ± 0.038</td>
<td>953.9 ± 13.1</td>
<td>962.8 ± 13.2</td>
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</tbody>
</table>

$T = (473.35 ± 0.12)$ K, $p = (17.5144 ± 0.0044)$ MPa
$k_{cell} = (0.06482 ± 0.00011)$ cm$^{-1}$
$\kappa_{w}^{exp} = (3.7682 ± 0.0037) \cdot 10^{-6}$ S·cm$^{-1}$

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<td>NaCl(aq)</td>
<td>1086.32 ± 0.16</td>
<td>922.91 ± 0.16</td>
<td>678.90 ± 3.10</td>
<td>735.6 ± 3.3</td>
<td>760.4 ± 3.4</td>
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<tr>
<td>HAc(aq)</td>
<td>9041.0 ± 1.2</td>
<td>7677.7 ± 1.2</td>
<td>135.36 ± 0.16</td>
<td>17.630 ± 0.021</td>
<td>1202.3 ± 18.0</td>
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<tr>
<td>NaAc(aq)</td>
<td>582.373 ± 0.088</td>
<td>494.760 ± 0.088</td>
<td>313.30 ± 0.37</td>
<td>629.40 ± 0.76</td>
<td>647.18 ± 0.78</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>1654.3 ± 4.0</td>
<td>1405.5 ± 4.0</td>
<td>1806.7 ± 6.9</td>
<td>1285.4 ± 5.9</td>
<td>1315.5 ± 6.0</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>1332.6 ± 17.0</td>
<td>1132.2 ± 17.0</td>
<td>1121.5 ± 3.4</td>
<td>990.6 ± 13.2</td>
<td>1021.6 ± 13.7</td>
</tr>
</tbody>
</table>

$T = (498.17 ± 0.10)$ K, $p = (20.8206 ± 0.0046)$ MPa
$k_{cell} = (0.065088 ± 0.000059)$ cm$^{-1}$
$\kappa_{w}^{exp} = (4.1109 ± 0.0048) \cdot 10^{-6}$ S·cm$^{-1}$
Table 3.1. Continued

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<th>Solute</th>
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<th>$\Lambda^{exp}$</th>
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<td>S·cm²·mol⁻¹</td>
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<tr>
<td>NaCl(aq)</td>
<td>112.13 ± 0.15</td>
<td>90.9 ± 0.15</td>
<td>77.65 ± 0.18</td>
<td>854.4 ± 2.2</td>
<td>863.8 ± 2.3</td>
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<tr>
<td>HAc(aq)</td>
<td>141.08 ± 0.13</td>
<td>114.3 ± 0.13</td>
<td>11.367 ± 0.021</td>
<td>99.42 ± 0.18</td>
<td>1250.0 ± 16.7</td>
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<tr>
<td>NaAc(aq)</td>
<td>157.98 ± 0.14</td>
<td>128.04 ± 0.14</td>
<td>92.580 ± 0.080</td>
<td>731.26 ± 0.86</td>
<td>741.38 ± 0.87</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>202.25 ± 0.62</td>
<td>163.9 ± 0.62</td>
<td>222.91 ± 0.17</td>
<td>1359.9 ± 4.3</td>
<td>1372.4 ± 4.3</td>
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<tr>
<td>NaOH(aq)</td>
<td>177.6 ± 2.4</td>
<td>143.9 ± 2.4</td>
<td>151.369 ± 0.069</td>
<td>1051.9 ± 14.3</td>
<td>1065.5 ± 14.5</td>
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</table>

$T = (525.32 \pm 1.4)$ K, $p = (17.4945 \pm 0.0026)$ MPa
$k_{cell} = (0.06501 \pm 0.00077)$ cm⁻¹
$\kappa_{w}^{exp} = (4.4887 \pm 0.0040) \cdot 10^{-6}$ S·cm⁻¹

<table>
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<tr>
<th>Solute</th>
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<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
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<tr>
<td></td>
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</tr>
<tr>
<td>NaCl(aq)</td>
<td>1086.32 ± 0.16</td>
<td>846.44 ± 0.16</td>
<td>735.1 ± 1.5</td>
<td>868.4 ± 1.8</td>
<td>899.1 ± 1.9</td>
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<tr>
<td>HAc(aq)</td>
<td>9041.1 ± 1.2</td>
<td>7041.4 ± 1.2</td>
<td>80.055 ± 0.048</td>
<td>11.3692 ± 0.0069</td>
<td>1283.4 ± 19.4</td>
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<tr>
<td>NaAc(aq)</td>
<td>582.373 ± 0.088</td>
<td>453.760 ± 0.088</td>
<td>332.8 ± 1.3</td>
<td>736.3 ± 2.9</td>
<td>757.8 ± 3.0</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>1654.3 ± 4.0</td>
<td>1289.1 ± 4.0</td>
<td>1788.8 ± 6.7</td>
<td>1387.7 ± 6.2</td>
<td>1424.7 ± 6.4</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>1332.6 ± 17.0</td>
<td>1038.4 ± 17.0</td>
<td>1132.6 ± 4.6</td>
<td>1090.7 ± 14.9</td>
<td>1130.9 ± 15.4</td>
</tr>
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</table>

*After publication, errors in the calculation of values of $\Lambda^o$ were discovered, and subsequently corrected. The original tables reported in Erickson et al. (2011) are in the Appendix, Table C.1
Table 3.2. Values of experimental molar conductivities, $\Lambda^{\text{exp}}$, and fitted limiting molar conductivities, $\Lambda^*$, for NaCl(aq), DAc(aq), NaAc(aq), DCl(aq), and NaOD(aq) in D$_2$O from $T = 368$ K to $T = 548$ K at $p = 20$ MPa

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
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<th>$\Lambda^{\text{exp}}$</th>
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<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>45.500 ± 0.087</td>
<td>50.583 ± 0.087</td>
<td>48.950 ± 0.087</td>
<td>15.259 ± 0.014</td>
<td>311.73 ± 0.6</td>
<td>313.45 ± 0.61</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>550.60 ± 0.58</td>
<td>612.11 ± 0.58</td>
<td>592.31 ± 0.58</td>
<td>29.952 ± 0.015</td>
<td>50.568 ± 0.054</td>
<td>575.7 ± 6.2</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>118.59 ± 0.13</td>
<td>131.84 ± 0.13</td>
<td>127.58 ± 0.13</td>
<td>30.9123 ± 0.018</td>
<td>242.68 ± 0.28</td>
<td>245.21 ± 0.29</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>364.2 ± 1.6</td>
<td>404.9 ± 1.6</td>
<td>391.8 ± 1.6</td>
<td>249.66 ± 0.32</td>
<td>637.2 ± 2.7</td>
<td>643.9 ± 2.4</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>162.8 ± 1.7</td>
<td>181.0 ± 1.7</td>
<td>175.1 ± 1.7</td>
<td>63.422 ± 0.038</td>
<td>362.2 ± 3.5</td>
<td>365.6 ± 3.5</td>
</tr>
</tbody>
</table>

$T = (368.601 ± 0.045)$ K, $p = (17.5825 ± 0.0029)$ MPa

$\kappa_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_{\text{w exp}} = (5.1157 ± 0.0042) \cdot 10^{-6}$ S·cm$^{-1}$

$T = (422.40 ± 0.10)$ K, $p = (17.5023 ± 0.0035)$ MPa

$\kappa_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_{\text{w exp}} = (8.2487 ± 0.0058) \cdot 10^{-6}$ S·cm$^{-1}$
Table 3.2.  Continued

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<th>$\Lambda^{exp}$</th>
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<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>105.48 ± 0.11</td>
<td>117.26 ± 0.11</td>
<td>102.43 ± 0.11</td>
<td>55.641 ± 0.094</td>
<td>543.2 ± 1.0</td>
<td>549.4 ± 1.1</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>983.1 ± 0.60</td>
<td>1092.92 ± 0.60</td>
<td>954.62 ± 0.60</td>
<td>29.427 ± 0.017</td>
<td>30.826 ± 0.025</td>
<td>1010.7 ± 9.7</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>198.26 ± 0.14</td>
<td>220.41 ± 0.14</td>
<td>192.53 ± 0.14</td>
<td>101.89 ± 0.14</td>
<td>532.99 ± 0.81</td>
<td>541.00 ± 0.83</td>
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<tr>
<td>DCI(aq)</td>
<td>824.2 ± 3.0</td>
<td>916.3 ± 3.0</td>
<td>800.4 ± 3.0</td>
<td>797.9 ± 1.3</td>
<td>996.9 ± 3.6</td>
<td>1019.1 ± 3.7</td>
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<tr>
<td>NaOD(aq)</td>
<td>443.9 ± 4.2</td>
<td>493.4 ± 4.2</td>
<td>431.0 ± 4.2</td>
<td>336.16 ± 0.21</td>
<td>779.9 ± 6.6</td>
<td>794.5 ± 6.8</td>
</tr>
</tbody>
</table>

$T = (473.35 \pm 0.12) \text{ K, } p = (17.5144 \pm 0.0044) \text{ MPa}$

$k_{cell} = (0.06482 \pm 0.00011) \text{ cm}^{-1}$

$\kappa_{w}^{exp} = (14.4543 \pm 0.0061) \cdot 10^{-6} \text{ S·cm}^{-1}$

NaCl(aq)   | 669.342 ± 0.093  | 744.116 ± 0.093      | 629.870 ± 0.093  | 352.7 ± 2.1               | 560.0 ± 3.3       | 577.4 ± 3.4     |
| DAc(aq)    | 68206.1 ± 8.8    | 75825.5 ± 8.8        | 63946.5 ± 8.8   | 193.91 ± 0.14              | 3.0324 ± 0.0022   | 1038.1 ± 17.1   |
| NaAc(aq)   | 794.706 ± 0.098  | 883.485 ± 0.098      | 747.820 ± 0.098  | 417.62 ± 0.52              | 565.47 ± 0.70     | 583.81 ± 0.72   |
| DCI(aq)    | 4284.0 ± 13.0    | 4762.5 ± 13.0        | 4031.3 ± 13.0   | 3950.0 ± 47.9              | 979.8 ± 12.2      | 1031.6 ± 12.9   |
| NaOD(aq)   | 2276.9 ± 20.0    | 2531.3 ± 20.0        | 2142.7 ± 20.0   | 1634.6 ± 6.2               | 762.8 ± 6.7       | 797.7 ± 7.1     |

$T = (498.17 \pm 0.10) \text{ K, } p = (20.8206 ± 0.0046) \text{ MPa}$

$k_{cell} = (0.065088 ± 0.000059) \text{ cm}^{-1}$

$\kappa_{w}^{exp} = (14.947 ± 0.011) \cdot 10^{-6} \text{ S·cm}^{-1}$

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<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
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<td>NaCl(aq)</td>
<td>669.342 ± 0.093</td>
<td>744.116 ± 0.093</td>
<td>629.870 ± 0.093</td>
<td>352.7 ± 2.1</td>
<td>560.0 ± 3.3</td>
<td>577.4 ± 3.4</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>68206.1 ± 8.8</td>
<td>75825.5 ± 8.8</td>
<td>63946.5 ± 8.8</td>
<td>193.91 ± 0.14</td>
<td>3.0324 ± 0.0022</td>
<td>1038.1 ± 17.1</td>
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<tr>
<td>NaAc(aq)</td>
<td>794.706 ± 0.098</td>
<td>883.485 ± 0.098</td>
<td>747.820 ± 0.098</td>
<td>417.62 ± 0.52</td>
<td>565.47 ± 0.70</td>
<td>583.81 ± 0.72</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>4284.0 ± 13.0</td>
<td>4762.5 ± 13.0</td>
<td>4031.3 ± 13.0</td>
<td>3950.0 ± 47.9</td>
<td>979.8 ± 12.2</td>
<td>1031.6 ± 12.9</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>2276.9 ± 20.0</td>
<td>2531.3 ± 20.0</td>
<td>2142.7 ± 20.0</td>
<td>1634.6 ± 6.2</td>
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<td>797.7 ± 7.1</td>
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<td>S·cm²·mol⁻¹</td>
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<tr>
<td>NaCl(aq)</td>
<td>91.13 ± 0.11</td>
<td>101.31 ± 0.11</td>
<td>81.74 ± 0.11</td>
<td>55.37 ± 0.10</td>
<td>677.5 ± 1.5</td>
<td>685.9 ± 1.5</td>
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<tr>
<td>DAc(aq)</td>
<td>509.34 ± 0.56</td>
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<td>456.8 ± 0.56</td>
<td>11.898 ± 0.017</td>
<td>26.043 ± 0.025</td>
<td>1064.5 ± 9.9</td>
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<td>NaAc(aq)</td>
<td>156.10 ± 0.13</td>
<td>173.54 ± 0.13</td>
<td>140.02 ± 0.13</td>
<td>84.39 ± 0.95</td>
<td>625.34 ± 0.61</td>
<td>635.24 ± 0.62</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>333.3 ± 1.4</td>
<td>370.6 ± 1.4</td>
<td>299.0 ± 1.4</td>
<td>327.72 ± 0.28</td>
<td>1096.1 ± 4.4</td>
<td>1115.1 ± 4.4</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>351.3 ± 3.4</td>
<td>390.5 ± 3.4</td>
<td>315.1 ± 3.4</td>
<td>273.97 ± 0.27</td>
<td>869.5 ± 7.6</td>
<td>886.9 ± 7.8</td>
</tr>
</tbody>
</table>

$T = (525.32 ± 1.4) \text{ K}, \ p = (17.4945 ± 0.0026) \text{ MPa}$

$k_{cell} = (0.06501 ± 0.00077) \text{ cm}^{-1}$

$\kappa_{w, exp} = (16.0201 ± 0.0047) \cdot 10^{-6} \text{ S·cm}^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^{o*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg⁻¹</td>
<td>mol·kg⁻¹</td>
<td>mol·L⁻¹</td>
<td>S·cm⁻¹</td>
<td>S·cm²·mol⁻¹</td>
<td>S·cm²·mol⁻¹</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>651.680 ± 0.093</td>
<td>724.481 ± 0.093</td>
<td>561.420 ± 0.093</td>
<td>383.3 ± 2.1</td>
<td>682.7 ± 3.7</td>
<td>706.7 ± 3.8</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>68206.1 ± 8.8</td>
<td>75825.5 ± 8.8</td>
<td>58547.7 ± 8.8</td>
<td>117.703 ± 0.071</td>
<td>2.0104 ± 0.0012</td>
<td>1158.5 ± 13.7</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>794.706 ± 0.098</td>
<td>883.485 ± 0.098</td>
<td>684.630 ± 0.098</td>
<td>416.2 ± 1.3</td>
<td>615.1 ± 1.9</td>
<td>640.1 ± 1.9</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>685.3 ± 2.5</td>
<td>761.8 ± 2.5</td>
<td>590.4 ± 2.5</td>
<td>708.8 ± 1.7</td>
<td>1200.5 ± 4.9</td>
<td>1225.2 ± 5.1</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>2276.9 ± 20.0</td>
<td>2531.3 ± 20.0</td>
<td>1961.8 ± 2.0</td>
<td>1806.0 ± 6.8</td>
<td>920.6 ± 8.1</td>
<td>967.5 ± 8.6</td>
</tr>
</tbody>
</table>

$T = (548.44 ± 0.10) \text{ K}, \ p = (20.7406 ± 0.0079) \text{ MPa}$

$k_{cell} = (0.065055 ± 0.000059) \text{ cm}^{-1}, k_{cell} = (0.06477 ± 0.00011) \text{ cm}^{-1}$ (for DCI)

$\kappa_{w, exp} = (15.3062 ± 0.0084) \cdot 10^{-6} \text{ S·cm}^{-1}$

*After publication, errors in the calculation of values of $\Lambda^{o}$ were discovered, and subsequently corrected. The original tables reported in Erickson et al. (2011) are in the Appendix, Table C.2
3.2, were used to calculate values of $\Lambda_{NaOH}$ and $\Lambda_{NaOD}$, at the concentration of OH$^-$/OD$^-$ shown by reaction (3.11). We used these values to calculate values of $\lambda$ for OH$^-$ and OD$^-$ using values of $\lambda_{Na+}$ ($\Lambda_{NaOH} = [\lambda_{Na^+} + \lambda_{OH^-}]$), which have been calculated from Marshall’s (1987b) reduced state relationship. These values were then used to calculate values of $\kappa_{OH-/OD-}$. Values of $\kappa_{OH-/OD-}$ were then subtracted from the measured values of $\kappa$ for NaAc in order to calculate corrected values, $\kappa_{corr}$, for NaAc: $\kappa_{corr} = \kappa_{NaAc} - \kappa_{OH-/OD-}$. Values of the calculated degree of hydrolysis at each temperature, $\alpha_{hyd}$, and the corrected values of $\Lambda_{NaAc} = [\lambda_{Na^+} + \lambda_{Ac^-}]$, are listed in Part II of Appendix C, Tables C.10 and C.11. In all cases, the correction was less than 1 percent. Equation (3.9) was then used, as described above, to determine the limiting molar conductivities of NaAc: $\Lambda_{NaAc}^\circ = [\lambda_{Na^+}^\circ + \lambda_{Ac^-}^\circ]$ in H$_2$O and D$_2$O. The values for the limiting conductance for each acid and electrolyte in H$_2$O and D$_2$O, derived from this fitting procedure, are tabulated in Tables 3.1 and 3.2.

3.4.2 Values of $pK_{aq}$ and $\Delta pK_{aq}$

Table 3.3 reports the experimental ionization constants of acetic acid in both H$_2$O and D$_2$O. Original values reported by Erickson et al. (2011) are reported in Part I of Appendix C, Table C.3. Although, the values calculated from our conductance results, using equation (3.3), are expressed in terms of the hypothetical 1 molar standard state, $K_c$, we have chosen to report these results in terms of the aquamolal standard state, $K_{aq}$. Uncertainties were calculated as the root mean sum of squares, as discussed in Appendix D.
Table 3.3. Calculated values of $K_{aq}$, $pK_{aq}$ and $\Delta pK_{aq}$ for HAc and DAc from $T = 368$ K to $T = 548$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$K_{aq} \cdot 10^6$</th>
<th>$pK_{aq}$ (HAc)</th>
<th>$pK_{aq}$ (DAc)</th>
<th>$\Delta pK_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>368.601 ± 0.045</td>
<td>17.5825 ± 0.0029</td>
<td>13.77 ± 0.21</td>
<td>5.120 ± 0.057</td>
<td>4.8610 ± 0.0064</td>
<td>5.2908 ± 0.0046</td>
</tr>
<tr>
<td>422.40 ± 0.10</td>
<td>17.5023 ± 0.0035</td>
<td>7.08 ± 0.11</td>
<td>2.579 ± 0.030</td>
<td>5.1501 ± 0.0061</td>
<td>5.5885 ± 0.0046</td>
</tr>
<tr>
<td>473.35 ± 0.12</td>
<td>17.5144 ± 0.0044</td>
<td>2.903 ± 0.042</td>
<td>1.036 ± 0.010</td>
<td>5.5371 ± 0.0062</td>
<td>5.9847 ± 0.0041</td>
</tr>
<tr>
<td>498.17 ± 0.10</td>
<td>20.8206 ± 0.0046</td>
<td>1.923 ± 0.034</td>
<td>0.628 ± 0.014</td>
<td>5.7160 ± 0.0064</td>
<td>6.2021 ± 0.0071</td>
</tr>
<tr>
<td>525.32 ± 1.4</td>
<td>17.4945 ± 0.0026</td>
<td>0.962 ± 0.019</td>
<td>0.3442 ± 0.0036</td>
<td>6.017 ± 0.010</td>
<td>6.4632 ± 0.0044</td>
</tr>
<tr>
<td>548.44 ± 0.10</td>
<td>20.7406 ± 0.0079</td>
<td>0.698 ± 0.012</td>
<td>0.2217 ± 0.0032</td>
<td>6.1559 ± 0.0065</td>
<td>6.6543 ± 0.0050</td>
</tr>
</tbody>
</table>

*After publication, errors in the calculation of values of $K_{aq}$, $pK_{aq}$ and $\Delta pK_{aq}$ were discovered, and subsequently corrected. The original tables reported in Erickson et al. (2011) are in the Appendix, Table C.3
3.5 Discussion

3.5.1 Comparison of Values of $\Lambda^\circ$

The experimental values for $\log[\Lambda^\circ]$, from Tables 3.1 and 3.2, are plotted in Figures 3.1 and 3.2 as a function of $\log[\eta_w]$, where $\eta_w$ is the viscosity of the solvent, in P. All of the experimental values of $\Lambda^\circ$ consistently increase with temperature in both solvents, as expected from the Stokes-Einstein equation, and the sequence of values for each solute at each temperature is the same. However, the magnitudes of $\Lambda_{\text{HCl}}^\circ$, $\Lambda_{\text{HAc}}^\circ$, $\Lambda_{\text{NaCl}}^\circ$ and $\Lambda_{\text{NaOH}}^\circ$ are all greater in light water than the corresponding values in heavy water.

The dependence of limiting molar conductivities on temperature and pressure can be described by a number of models. Marshall (1987b) devised a reduced state relationship, based on the observation that $\Lambda^\circ$ approaches a limiting value at zero density, which is common to all electrolytes for which data were available. An alternative approach was taken by Oelkers and Helgeson (1988) who reported a model based on an Arrhenius model for the conduction process. Zimmerman et al. (2007, 2009) reported that values of $\Lambda^\circ$ could be accurately represented by simple empirical functions of the solvent viscosity, equation (1.44). This method was reported to be superior for fitting experimental data (up to 523 K for NaCl and 573 K for HCl), when compared to the reduced density method of Marshall and the Arrhenius method of Oelkers and Helgeson. More recently, Zimmerman et al. (2012a, 2012b) have revised equation (1.44), to include a solvent density term, $\rho_w$, equation (1.45):

$$
\log[\Lambda^\circ] = \log[A_i] + \left( A_i + \frac{A_i}{\rho_w} \right) \log[\eta_w] \tag{3.12}
$$
Figure 3.1. Plots of \( \log[\Lambda^\circ] \) as a function of \( \log[\eta_{\text{H}_2\text{O}}] \): (□) NaCl; (●) NaAc; (△) HCl; and (●) NaOH in H\(_2\)O. The solid lines represent fits to equation (3.12).
Figure 3.2. Plots of \( \log[\Lambda^0] \) as a function of \( \log[\eta_{\text{D}_2\text{O}}] \): (□) NaCl; (●) NaAc; (△) DCl; and (●) NaOD in D\(_2\)O. The solid lines represent fits to equation (3.12)
For each species in H\textsubscript{2}O and D\textsubscript{2}O, equation (3.12) was fitted to the temperature- and pressure-dependent experimental values of \( \Lambda^o \) reported in Tables 3.1 and 3.2, along with values of \( \Lambda^o \) reported previously in the literature at 298.15 K. The value of \( \Lambda^o \) for NaCl in H\textsubscript{2}O at 298.15 K was obtained from Bešter-Rogač \textit{et al.} (1999). The value of \( \Lambda^o \) for NaCl in D\textsubscript{2}O at 298.15 K was taken from Swain and Evans (1966). The value of \( \Lambda^o \) for NaAc in H\textsubscript{2}O at 298.15 K was calculated from the study of MacInnes and Shedlovsky (1932) (as regressed by Zimmerman and Wood, 1992). The value of \( \Lambda^o \) for NaAc in D\textsubscript{2}O at 298.15 K came from Brescia \textit{et al.} (1940). Values of \( \Lambda^o \) for HCl and DCl at 298.15 K were obtained from Stokes (1962) and Tada \textit{et al.} (1992), respectively. Finally, values of \( \Lambda^o \) for NaOH and NaOD at 298.15 K were obtained from Marsh and Stokes (1964) and Tada \textit{et al.} (1993), respectively. A weighted regression was used, whereby data at 298.15 K were assigned an uncertainty between \( \pm 0.1 \) and \( \pm 0.4 \) percent, and the high-temperature flow results were assigned an uncertainty of \( \pm 3 \) percent. The results are plotted in Figures 3.1 and 3.2, and values of the adjustable parameters, \( A_1 \) to \( A_3 \), are tabulated in Table 3.4.

The limiting molar conductivities from this study are compared with those of previous workers in Figure 3.3, which plots the relative deviation of the experimental values of \( \Lambda^o \) in light-water, with values previously reported in the literature and expressions reported by Zimmerman and Wood (2002), which were derived by fitting Marshall's (1987b) reduced density model to their own data, plus a limited number of other literature results. Values of \( \Lambda^o \) for NaCl have been measured by from 523 to 623 K by Ho \textit{et al.} (2000a) and from 288 to 318 K by Gunning and Gordon (1942). Values of \( \Lambda^o \) for HCl have been reported from 373 to 623 K by Ho \textit{et al.} (2001) and from 278 to
Table 3.4. Fitted parameters for the temperature dependence of limiting molar conductivities, $\Lambda^\circ$, of NaCl, NaAc, HCl/DCl and NaOH/NaOD in H$_2$O and D$_2$O, according to equation (3.12)***

<table>
<thead>
<tr>
<th>Solute:</th>
<th>H$_2$O</th>
<th></th>
<th></th>
<th>D$_2$O</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1^*$</td>
<td>$A_2^*$</td>
<td>$A_3^{**}$</td>
<td>$A_1^*$</td>
<td>$A_2^*$</td>
<td>$A_3^{**}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>2.05 ± 0.22</td>
<td>-0.883 ± 0.017</td>
<td></td>
<td>6.78 ± 1.97</td>
<td></td>
<td>-0.683 ± 0.046</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>0.52 ± 0.19</td>
<td>-1.170 ± 0.099</td>
<td>0.088 ± 0.038</td>
<td></td>
<td>0.300 ± 0.050</td>
<td></td>
</tr>
<tr>
<td>HCl/DCl(aq)</td>
<td>34.03 ± 2.43</td>
<td>-0.607 ± 0.019</td>
<td>0.0522 ± 0.0075</td>
<td></td>
<td>31.91 ± 5.190</td>
<td></td>
</tr>
<tr>
<td>NaOH/NaOD(aq)</td>
<td>9.60 ± 3.78</td>
<td>-0.76 ± 0.11</td>
<td>0.051 ± 0.041</td>
<td></td>
<td>2.85 ± 1.05</td>
<td></td>
</tr>
</tbody>
</table>

*Both $A_1$ and $A_2$ are unit-less coefficients
**$A_3$ has units of cm$^3$.g$^{-1}$
***Uncertainty estimates are standard errors in the fitted coefficients
Figure 3.3. Comparison of experimental (exp.) and literature (lit.) values of $\Lambda^\circ$ as a function of $T$, as a relative % difference, for each solution: (□) NaCl; (♦) NaAc; (△) HCl; and (●) NaOH in H$_2$O.
Values of $\Lambda^\circ$ for NaOH have been reported from 373 to 623 K by Tada et al. (1992). Values of $\Lambda^\circ$ for NaOH have been reported from 373 to 623 K by Ho et al. (2000b) and from 348 to 373 K by Bianchi et al. (1994). Finally, values of $\Lambda^\circ$ for NaCH$_3$COO have been reported by Zimmerman and Wood (2002). In order to do a direct comparison of the values of $\Lambda^\circ$ reported in this thesis with those reported in the literature, literature values of $\log[\Lambda^\circ]$ for HCl, NaCl, NaOH and NaAc were plotted as a function of $\log[\eta_{H2O}]$:

$$\log[\Lambda^\circ] = a_L \cdot (\log[\eta_{H2O}])^2 + b_L \cdot \log[\eta_{H2O}] + c_L$$

(3.13)

Literature values of $\Lambda^\circ$ for each of HCl, NaCl, NaOH and NaAc were then calculated at the values of $\eta_{H2O}$, which corresponded to the experimental values of $T$ and $p$ reported in this thesis. Calculated values of $a_L$, $b_L$ and $c_L$ are reported below in Table 3.5. The experimental values of $\Lambda^\circ$ in Table 3.1 deviate from the literature results by no more than eight percent and, in most cases, by less than five percent. These differences may reflect systematic errors in the cell constant, which can arise from small changes in the dimensions of the cell over time, and the assumption that the theoretical expressions for $J_1$ and $J_2$ in the FHFP equation are accurate over our experimental range of concentrations. The agreement is therefore quite acceptable. Since almost all of our experimental values of $\Lambda^\circ$ for HCl, NaCl, NaOH and NaAc are more positive than the literature values, there is a partial cancellation of systematic errors that occurs when using these values of $\Lambda^\circ$ in equation (3.8) to calculate values of $[\lambda_{H^+^\circ} + \lambda_{Ac^-^\circ}]$, from which we calculated values of $pK_{aq}$. This was the purpose in adopting this experimental design.
Table 3.5. Parameters used in equation (3.13) to calculate the limiting molar conductivities, $\Lambda^\circ$, from literature values of $\Lambda^\circ$ of NaCl, NaAc, HCl and NaOH, in H$_2$O, at the same values of $\eta_{H2O}$ reported in this thesis.

<table>
<thead>
<tr>
<th>Solute:</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_L^*$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>-0.0119</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>-0.0357</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>-0.1441</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>-0.2088</td>
</tr>
</tbody>
</table>

*Coefficients $a_L$, $b_L$ and $c_L$ are unit-less.
3.5.2 Values of $pK_{aq}$ in H$_2$O

Figure 3.4 plots the experimental values of $pK_{aq}$ for acetic acid in H$_2$O at elevated temperatures, along with values reported by Mesmer et al. (1989) and Zimmerman and Wood (2002). Our experimental values of $pK_{aq}$ agree well with these authors. As was done by these authors, we chose to model the temperature and pressure dependence of all values of $pK_{aq}$ plotted in Figure 3.4, using the density model (Mesmer et al., 1988), equations (1.19) and (1.20):

$$\log[K_{aq}] = a_d + \frac{b_d}{T} + \frac{c_d}{T^2} + \frac{d_d}{T^3} + \left[ e_d + \frac{f_d}{T} + \frac{g_d}{T^2} \right] \cdot \log[\rho_{H2O}], \quad (3.14)$$

Here, the constants $a_d$ through $g_d$ are adjustable fitting parameters whose significance is discussed in Section 1.4.1.3, and $\rho_{H2O}$ is the density of water, taken from Wagner and Pruß (2002). Although parameters $b_d$ through $e_d$ were found to be of modest statistical significance, they were included here for better precision in reproducing the equilibrium constant data, and for consistency with Mesmer and Herting (1978). The fitted parameters are tabulated in Table 3.6, and the fit is plotted in Figure 3.4. The deviations between the fitted values of $pK_{aq}$ with the experimental values are plotted in Figure 3.5. The larger difference between my experimental points at 523 K compared to the fit is due to the use of a more dilute acetic acid solution ($\sim 10^{-4}$ mol·kg$^{-1}$). The deviation at 548 K is due to the experimental challenges associated with the high temperature since the results from this work, Mesmer et al. (1988) and Zimmerman and Wood (2002) all lie within the combined experimental uncertainties. The reason for the deviation from the fit at 368 K is unknown. In no case was the fitted deviation greater than $\pm 0.07$. 

135
Figure 3.4. Comparison of values of $pK_{aq}$ for CH$_3$COOH in H$_2$O as a function of $T$: (▲), this study; (△), Zimmerman and Wood (2002); (○), Mesmer et al., (1989).
Table 3.6. Fitted parameters obtained for the ionization constant of acetic acid in H$_2$O and D$_2$O as a function of temperature and solvent density, using equations (3.14) and (3.15).

<table>
<thead>
<tr>
<th>Parameter:</th>
<th>pK$_{aq}$</th>
<th>Parameter:</th>
<th>ΔpK$_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAc</td>
<td>DAc*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_d$</td>
<td>-20.38 ± 3.10</td>
<td>-21.83 ± 3.11</td>
<td>$Δa_d$</td>
</tr>
<tr>
<td>$b_d'10^3$/(K)</td>
<td>14.10 ± 3.16</td>
<td>13.97 ± 3.16</td>
<td>$Δb_d'10^3$/(K)</td>
</tr>
<tr>
<td>$c_d'10^6$/(K$^2$)</td>
<td>-4.20 ± 1.06</td>
<td>-4.20 ± 1.06</td>
<td>$Δc_d'10^6$/(K$^2$)</td>
</tr>
<tr>
<td>$d_d'10^8$/(K$^3$)</td>
<td>4.12 ± 1.16</td>
<td>4.12 ± 1.16</td>
<td>$Δd_d'10^8$/(K$^3$)</td>
</tr>
<tr>
<td>$e_d$</td>
<td>28.11 ± 10.31</td>
<td>29.75 ± 10.33</td>
<td>$Δe_d$</td>
</tr>
<tr>
<td>$f_d'10^3$/(K)</td>
<td>-3.04 ± 1.03</td>
<td>-3.04 ± 1.03</td>
<td>$Δf_d'10^3$/(K)</td>
</tr>
<tr>
<td>$g_d'10^6$/(K$^2$)</td>
<td>8.4 ± 2.6</td>
<td>8.4 ± 2.6</td>
<td>$Δg_d'10^6$/(K$^2$)</td>
</tr>
</tbody>
</table>

Relative Standard Error 0.0252 0.0347 Relative Standard Error 0.0238

*Parameters calculated for pK$_{aq,D2O} = pK_{aq,H2O} + ΔpK_{aq}$, eg. $a_d,DAc = a_d,HAc + Δa_d$. The standard uncertainty for pK$_{aq}(CH_3COOD)$ is calculated from the sum of the variances for pK$_{aq}(CH_3COOH)$ and ΔpK$_{aq}$.
Figure 3.5. Absolute deviation between the experimental values and fitted density model values of the $pK_{aq}$ of CH$_3$COOH in H$_2$O, $\Delta pK_{aq,CH3COOH} = pK_{aq,CH3COOH}^{exp} - pK_{aq,CH3COOH}^{pred}$, as a function of temperature.
3.5.3 Values of $\Delta pK_{aq}$

The experimental values of $pK_{aq}$ for HAc and DAc, reported in Table 3.3, are plotted in Figure 3.6 over the temperature range $T = 368$ K to $T = 548$ K. Experimental values of $\Delta pK_{aq} = [pK_{aq,DAc} - pK_{aq,HAc}]$ are plotted in Figures 3.7 and 3.8, along with the experimental uncertainties. Our experiments were designed to measure the difference in molar conductivity between solutions in D$_2$O vs. H$_2$O directly, so that most systematic errors would cancel. To maintain consistency with this approach, we chose to model our experimental values for $\Delta pK_{aq}$ directly, relative to the “density model” that was fitted to all the light water data, equation (3.14). Following Bulemela and Tremaine (2009), we used the following approximation: $\rho_{D2O} \approx \rho_{H2O}(M_{D2O}/M_{H2O})$ to yield the corresponding expression for $\Delta pK_{aq}$ ($\Delta pK_{aq} = -\Delta \log[K_{aq}]$):

$$
\Delta \log[K_{aq}] = \Delta a_d + \frac{\Delta b_d}{T} + [\Delta e_d] \cdot \log[\rho_{D2O}] + [e_d] \cdot \log\left[\frac{M_{D2O}}{M_{H2O}}\right],
$$

(3.15)

where the difference in the parameters $a_d$, $b_d$, and $e_d$ for D$_2$O are relative to H$_2$O. Here, $M_{H2O}$ and $M_{D2O}$ are the molar masses of H$_2$O and D$_2$O, respectively; $\Delta a$, $\Delta b$ and $\Delta e$ were used as adjustable parameters; parameter $e$ is the corresponding light water value in equation (3.14); and $\rho_{D2O}$ is the density of D$_2$O, calculated from the equation of state by Hill et al. (1982). Values of the parameters for $\Delta pK_{aq}$ in equation (3.15), fitted to the experimental data in Table 3.3, are tabulated in Table 3.6. The deviations between the fitted values of $\Delta pK_{aq}$ with our experimental values are plotted in Figure 3.9. Equation (3.14) models the un-weighted values of $pK_{aq}$ for light water from our measurements, to a relative precision of $\pm 0.026$ units ($\pm 6\%$ in $K_{aq}$) or over the entire temperature range of interest. This probably represents a realistic estimate of both systematic and statistical
Figure 3.6. Comparison of experimental and predicted values of $pK_{aq}$ for CH$_3$COOH in H$_2$O (○) and CH$_3$COOD in D$_2$O (□) as a function of $T$. The solid lines represent the predicted equations represented by equation (3.14) for CH$_3$COOH and the combination of equations (3.14) and (3.15) for CH$_3$COOD.
Figure 3.7. Comparison of values of $\Delta pK_{aq}$ for $\mathrm{CH}_3\mathrm{COOH}$ ($\mathrm{CH}_3\mathrm{COOD}$) (▲) from this study to $\mathrm{H}_2\mathrm{PO}_4^-$ ($\mathrm{D}_2\mathrm{PO}_4^-$) (□), as reported by Mesmer and Herting (1978), β-naphthol (⊗) and $\mathrm{B(OH)}_3$ ($\mathrm{B(OD)}_3$) (⊤), as reported by Bulemela and Tremaine (2009), and $\mathrm{HSO}_4^-$ ($\mathrm{DSO}_4^-$) (△), as reported by Lietzke and Stoughton (1963). The data point for $\mathrm{CH}_3\mathrm{COOH}$ ($\mathrm{CH}_3\mathrm{COOD}$) at 298.15 K was taken from Martin and Butler (1939).
Figure 3.8. Comparison of values of $\Delta pK_{aq}$ for $\text{CH}_3\text{COOH (CH}_3\text{COOD)}$ (▲) from this study to $\text{H}_2\text{PO}_4^-$ ($\text{D}_2\text{PO}_4^-$) (□), as reported by Mesmer and Herting (1978), and $\beta$-naphthol (○) and $\text{B(OH)}_3$ ($\text{B(OD)}_3$) (▼), as reported by Bulemela and Tremaine (2009) (expanded version). The data point for $\text{CH}_3\text{COOH (CH}_3\text{COOD)}$ at 298.15 K was taken from Martin and Butler (1939).
Figure 3.9. Absolute deviation between the experimental values and fitted density model values, equations (3.14) and (3.15), of the $\Delta p_{\text{aq}}$ of acetic acid, $[\Delta p_{\text{aq}}^{\text{expt}} - \Delta p_{\text{aq}}^{\text{pred}}]$, as a function of temperature.
uncertainties in this study. Using equation (3.15), we were able to reproduce values of ΔpK_{aq,} to within a relative precision of ± 0.024 units. Since the molar conductivities were determined by sequential measurements in our experimental design, most systematic errors were cancelled. Therefore, we estimate that equation (3.15) is accurate to ± 0.01 in ΔpK_{aq} or better. Calculated values of pK_{aq} for D_2O were obtained by adding calculated values of pK_{aq} obtained from equation (3.14) to those calculated values of ΔpK_{aq} in equation (3.15). These results are listed in Table 3.5, and plotted in Figure 3.6.

Figure 3.7 compares values of ΔpK_{aq} for acetic acid to other high-temperature high-pressure values of ΔpK_{aq} previously reported by Mesmer and Herting (1978), Lietzke and Stoughton (1963) and Bulemela and Tremaine (2009). The solid lines in Figure 3.7 are the calculated values of ΔpK_{aq}, which were obtained from equations (3.14) and (3.15). In agreement with the trend observed by Mesmer and Herting and Bulemela and Tremaine, the deuterium isotope effects at 423 K, exist at a value approximately 0.1 unit lower than that at 298 K, ΔpK_{aq} = 0.43 ± 0.01 vs. ΔpK_{aq} = 0.51 ± 0.01, but above 500 K, tend to swing up. This is consistent with the results reported by Bulemela and Tremaine (2009), but not those reported by Mesmer and Herting (1978).

We note that Lietzke and Stoughton (1963) and Mesmer and Herting (1978) report values of ΔpK_{a}, using molal units:

\[
\Delta pK_{aq} = \Delta pK_a - \log[1.1117] = \Delta pK_a - 0.0456
\]  

(3.16)
CHAPTER 4

DEUTERIUM ISOTOPE EFFECTS ON THE IONIZATION OF AQUEOUS PHOSPHORIC ACID FROM 298 K TO 571 K

4.1 Overview

Measurements of the ionization constants for phosphoric acid in light and heavy water, $K_{\text{H}_3\text{PO}_4}$ and $K_{\text{D}_3\text{PO}_4}$, from 298 to 571 K at $p = 20$ MPa, have been made using the state-of-the-art, high-temperature, high-pressure flow AC conductivity cell described in Chapter 2.

The measurements followed the experimental design discussed in Section 2.3.2, in which solutions of potassium chloride, phosphoric acid, potassium dihydrogen phosphate and hydrochloric acid, in both $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, were injected in sequence at each temperature and pressure. In doing so, systematic errors in the experimental molar conductivities of solutions in the two solvents canceled, thus yielding more precise values of the deuterium isotope effect, $\Delta pK_{\text{aq}}$.

4.2 Experimental

4.2.1 Solution Preparation

Aqueous stock solutions of $m = (1.1905 \pm 0.006) \text{ mol} \cdot \text{kg}^{-1} \text{H}_3\text{PO}_4$ in $\text{H}_2\text{O}$ and $m = (0.8679 \pm 0.001) \text{ mol} \cdot \text{kg}^{-1} \text{D}_3\text{PO}_4$ in $\text{D}_2\text{O}$ were prepared from stock solutions (Fisher Scientific, #A242P-500, 85 wt %) and (Sigma Aldrich, #176753, 85 wt % in $\text{D}_2\text{O}$, 98 atom % D), respectively, and standardized by titration against a standard NaOH solution at 298.15 K, to a relative precision of $\pm 0.1\%$. Stock solutions of $m = (0.1299 \pm 0.0003) \text{ mol} \cdot \text{kg}^{-1} \text{HCl}$ (Sigma Aldrich, #318965, 0.1 N standard), $m = (0.4677 \pm 0.0012) \text{ mol} \cdot \text{kg}^{-1}$
DCl (Sigma Aldrich, #543047, 35 wt % in D₂O, 99 atom % D), \( m = (0.2433 \pm 0.0013) \) mol·kg⁻¹ KOH (Fisher Scientific, #SS254-4, 50 wt %) and \( m = (0.1355 \pm 0.0005) \) mol·kg⁻¹ KOD (Sigma Aldrich, #176761, 40 wt % in D₂O, 98+ atom % D) were prepared from their sources by dilution. The HCl and DCl solutions were standardized by titration against a standard NaOH solution at 298.15 K and the KOH and KOD solutions were standardized by titration against potassium hydrogen phthalate (KHP, \( C_8H_4O_4K \), Fisher Scientific, #AC17712, 99.99%); previously dried at 403.15 K, to constant mass, and weighed to a relative precision of ± 0.002 %), also at 298.15 K to a relative precision of ± 0.1%. Stock solutions of \( m = 0.1163 \) mol·kg⁻¹ KCl (Fisher Scientific, #BP366-500, >99%) in H₂O and \( m = 0.1134 \) mol·kg⁻¹ KCl in D₂O, \( m = 0.1011 \) mol·kg⁻¹ KH₂PO₄ (Sigma Aldrich, #P0662, >99%) in H₂O, and \( m = 0.09297 \) mol·kg⁻¹ KD₂PO₄ (Sigma Aldrich, #329916, 98 atom % D) in D₂O were prepared by mass from their salts. KCl was dried at 573.15 K for 7 days, to constant mass, before use and weighed to a relative precision of ± 0.001 %. KH₂PO₄ was dried at 393.15 K to constant mass before use and weighed to a relative precision of ± 0.001 %.

D₂O (donated from Bruce Power, determined to be 99.730 mol % isotopically pure, see Section 2.1.3) was used in the preparation of the stock solutions in D₂O. The resistivity of the D₂O was tested before use with a Wissenschaftlich-Technische Werkstätten (WTW) model 3310 conductivity set meter, connected to a Lr 325/01 pure water conductivity dip probe (calibrated using a supplied, standard 5 \( \mu S \cdot cm^{-1} \) solution of KCl). It was found to be 2.1 MΩ·cm. The solutions in D₂O were prepared in a glove-bag flushed with Ar(g), which was continually kept under positive argon pressure, then stored under an atmosphere of argon until use. Nanopure water (resistivity 18.2 MΩ·cm) was
used to prepare the solutions in H$_2$O. Solutions in H$_2$O were kept under positive argon pressure in order to prevent contamination from atmospheric CO$_2$(g). Stock solutions were diluted to a concentration of $\sim 10^{-3}$ mol·kg$^{-1}$ by mass, to a relative precision of $\pm$ 0.01%, and stored in sealed Pyrex glass bottles.

### 4.2.2 AC Conductivity Measurements

AC impedance data were collected for the full series of solutions: H$_2$O, D$_2$O, KCl (in H$_2$O), KCl (in D$_2$O), H$_3$PO$_4$, D$_3$PO$_4$, KH$_2$PO$_4$ (in H$_2$O), KD$_2$PO$_4$ (D$_2$O), HCl, DCl, KOH, KOD, D$_2$O and H$_2$O, using the automatic injection system described in Section 2.2.3. A schematic of the injection sequence was shown in Figure 2.8. The result of these measurements was a series of values for the real and imaginary impedance, equation (1.58):

$$Z = Z_{Re} - j \cdot Z_{Im},$$

at frequencies of 100, 200, 500, 1000, 2000, 3000, 5000, 8000, and 10000 Hz. Values of $R_s$ for the solvents and each solution of interest were obtained by extrapolation of the impedance data collected, using the Hnedkovsky et al. (2005) extrapolation technique, described in Section 2.2.5. The Hnedkovsky method was chosen over the Nyquist plot method because it was found to be easier to use in extrapolating the impedance data to obtain values of $R_s$. Numerical values for the adjustable parameters in the equivalent circuit were determined through non-linear least-squares regression, using the Levenberg-Marquardt fitting algorithm. These were calculated for each species in H$_2$O, which are reported in Appendix Table E.1, and for each species in D$_2$O, which are reported in Appendix Table E.2. Comparisons of experimental and predicted values of $Z_{Re}$ as a
function of \(\frac{1}{f_{aw}}\), as well as the extrapolations to \(R_3\), each species in \(H_2O\) and \(D_2O\) are shown in Appendix Figures E.1 to E.48.

4.3 Methodology

Phosphoric acid, a weak electrolyte, and ionizes in aqueous solution according to the reaction:

\[
H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-
\]

\[c(1-\alpha) \quad \alpha \cdot c \quad \alpha \cdot c\]  

(4.2)

where \(\alpha\) is the degree of ionization. Further ionization takes place according to the reactions:

\[
H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}
\]

(4.3)

\[
HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}
\]

(4.4)

However, the second and third degrees of ionization are negligible in comparison to \(\alpha\).

The degree of ionization, \(\alpha\), in a solution of concentration, \(c\), is used to determine the equilibrium constant that we seek to measure (equation (2.15)):

\[
K_\alpha = \frac{(\alpha)^2 \cdot c \cdot \gamma^2}{(1-\alpha)}
\]

(4.5)

Values of \(c\) are calculated from equations (1.88) and (1.89):

\[
c = \frac{m \cdot \rho \cdot w_1}{w_1 + w_2}
\]

(4.6)

\[
\rho = \frac{(M_z \cdot \rho_w \cdot m) + (1000 \cdot \rho_w)}{(V^\circ \cdot \rho_w \cdot m) + 1000}
\]

(4.7)
To calculate values of $V^\circ$ for the strong electrolytes: KCl, KH$_2$PO$_4$, HCl and KOH, we summed values of $V^\circ$ for the corresponding ions, which were obtained from the SUPCRT program reported by Johnson et al. (1992). These are assumed to be the same for species in both H$_2$O and D$_2$O. For H$_3$PO$_4$, values of $V^\circ$ had to be calculated from the degree of dissociation, $\alpha$, equation (2.22):

$$V^\circ = \alpha \cdot V_{H_2PO_4}^\circ + \alpha \cdot V_{H^+}^\circ + (1 - \alpha) \cdot V_{H_3PO_4}^\circ,$$  \hspace{1cm} (4.8)

where $V^\circ$ for H$^+$ is taken to be zero. To do this, we used the assumption of Gruszkiewicz and Wood (1997), that the value of $\rho$ for the weak acid and $\rho_w$ for the solvent are the same, in order to estimate a value of $\alpha$ for the weak acid in H$_2$O and D$_2$O. Then, using this estimated value of $\alpha$, the actual value of $c$ for phosphoric acid in each solvent is calculated using equations (4.6) and (4.7). Values of $\rho$ and $\rho_w$ are compared for each solution in H$_2$O and D$_2$O as a function of temperature in Appendix Table E.3 and E.4, respectively, to prove that the two values differ only marginally, so that a second iteration was not necessary. Appendix Table E.5 reports values of $V^\circ$ for each species at our experimental conditions in H$_2$O (which are assumed to be the same in D$_2$O).

According to equations (2.16) and (2.17):

$$\alpha = \frac{\Lambda_{\text{exp}}}{\lambda_{H^+} + \lambda_{H_2PO_4}},$$  \hspace{1cm} (4.9)

and:

$$\lambda_{H^+} + \lambda_{H_2PO_4} = \Lambda_{KH_2PO_4} - \Lambda_{KCl} + \Lambda_{HCl},$$  \hspace{1cm} (4.10)

so that values of $\alpha$ for H$_3$PO$_4$ can be calculated from the experimental values of $\Lambda$ for H$_3$PO$_4$ and experimental values of $\Lambda$ for HCl, KCl and KH$_2$PO$_4$. It is known that HCl and KCl are strong electrolytes that fully dissociate under these conditions (Ho et al.,
Aqueous KH$_2$PO$_4$ however, undergoes a modest degree of amphiprotic ionization which requires a correction (discussed below).

To correct for small differences in the concentrations of solutions of KCl, HCl and KH$_2$PO$_4$, we used the FHFP model, equation (1.71):

$$\Lambda = \Lambda^\circ - S \cdot c^{1/2} + E \cdot c \cdot \ln[c] + J_1 \cdot c^{1/2} - J_2 \cdot c^{3/2}, \quad (4.11)$$

to calculate values of $\Lambda^\circ$ for H$_3$PO$_4$ from values of $\Lambda^\circ$ for KCl, HCl and KH$_2$PO$_4$.

Values of $K_a$ were calculated from equation (4.5), using values of $\alpha$, which were calculated by iteratively by combining equation (4.9) with equation (2.20):

$$\Lambda^{\text{exp}} = \alpha \cdot \left[ \Lambda^\circ - S \cdot (\alpha \cdot c)^{1/2} + E \cdot (\alpha \cdot c) \cdot \ln[\alpha \cdot c] + J_1 \cdot (\alpha \cdot c) - J_2 \cdot (\alpha \cdot c)^{3/2} \right] \quad (4.12)$$

where the terms $S$, $E$, $J_1$ and $J_2$ are defined by equations (1.72) to (1.84). Equations (1.72) to (1.84) require known values of solvent density, viscosity and dielectric constant. Values of $\rho_{H2O}$ were obtained from Wagner and Pruß (2002) using the ASME (version 10.0) database, and values of $\rho_{D2O}$ were obtained from Hill, et al. (1982) and Kestin and Sengers (1986) using the REFPROP (version 8.0) database. Values of $\eta_{H2O}$ and $\eta_{D2O}$ were also obtained from the ASME (version 10.0) and REFPROP (version 8.0) databases, respectively. Values of $\varepsilon_{H2O}$ were obtained from Fernández et al. (1997). Values of $\varepsilon_{D2O}$ were calculated using the method of Trevani et al. (2007), where values of $\varepsilon_{H2O}$ and $\varepsilon_{D2O}$ are assumed to be equal at the same number density at the same temperature. Values of $\rho$, $\eta$ and $\varepsilon$ for each solvent at each of the temperature and pressure conditions are reported in Appendix Table E.6.
4.4 Results

4.4.1 Values of \( \Lambda \) and \( \Lambda^0 \)

Experimental values for the cell corrected specific conductivity, \( \kappa_{\text{corr}} \), of each solution; the corresponding molar conductivity, \( \Lambda^\text{exp} \); and the cell constants, \( k_{\text{cell}} \), are reported in Tables 4.1 and 4.2 below. The concentrations are tabulated in Tables 4.1 and 4.2 as both aquamolarities, \( m_{\text{aq}} = \text{(mol solute)} \cdot (55.509 \text{ mol solvent})^{-1} \), equation (1.90), and calculated molarities, \( c = \text{(mol solute)} \cdot (\text{L solution})^{-1} \), equation (4.6).

Values of the limiting conductance for each of the salt solutions, \( \Lambda^0 \), were calculated from the FHFP model, using values for the distance of closest approach set equal to the Bjerrum distance, equation (1.84). The determination of \( \lambda_{\text{K}^+}^0 + \lambda_{\text{H}_2\text{PO}_4^-}^0 \) from \( \Lambda_{\text{KH}_2\text{PO}_4} \) was complicated by the amphiprotic ionization of the phosphate anion, according to the following reaction:

\[
2 \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_3\text{PO}_4^0 + \text{HPO}_4^{2-} \tag{4.13}
\]

To address this concern, values of \( \Lambda_{\text{KH}_2\text{PO}_4} \) were corrected, in accordance with the equilibrium in equation (4.13):

\[
m_{\text{aq,H}_3\text{PO}_4} = \frac{m_{\text{aq,H}^+} \cdot m_{\text{aq,H}_2\text{PO}_4^-}}{K_1} \tag{4.14}
\]

\[
m_{\text{aq,HPO}_4^{2-}} = \frac{K_2 \cdot m_{\text{aq,H}_2\text{PO}_4^-}}{m_{\text{aq,H}^+}} \tag{4.15}
\]

and the concentration of \( \text{OH}^- \), \( m_{\text{aq,OH}^-} \), can be represented through the auto-ionization of water, \( K_w \).
Table 4.1. Values of experimental molar conductivities, $\Lambda^{\text{exp}}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for KCl(aq), $\text{H}_3\text{PO}_4$ (aq), KH$_2$PO$_4$ (aq), HCl(aq), and KOH(aq) in H$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$ (mol·kg$^{-1}$)</th>
<th>$c \cdot 10^6$ (mol·L$^{-1}$)</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$ (S·cm$^{-1}$)</th>
<th>$\Lambda^{\text{exp}}$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\Lambda^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl(aq)</td>
<td>$1269.06 \pm 0.49$</td>
<td>$1276.58 \pm 0.49$</td>
<td>$187.55 \pm 0.66$</td>
<td>$146.91 \pm 0.52$</td>
<td>$150.23 \pm 0.53$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4$ (aq)</td>
<td>$2626.8 \pm 14.8$</td>
<td>$2642.3 \pm 14.9$</td>
<td>$807.5 \pm 1.9$</td>
<td>$305.6 \pm 1.9$</td>
<td>$379.7 \pm 1.7$</td>
</tr>
<tr>
<td>KH$_2$PO$_4$ (aq)</td>
<td>$1154.53 \pm 0.36$</td>
<td>$1161.37 \pm 0.37$</td>
<td>$118.98 \pm 0.13$</td>
<td>$102.34 \pm 0.12$</td>
<td>$105.12 \pm 0.12$</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>$912.9 \pm 2.3$</td>
<td>$918.3 \pm 2.3$</td>
<td>$385.63 \pm 0.26$</td>
<td>$419.9 \pm 1.1$</td>
<td>$424.8 \pm 1.1$</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>$2523.3 \pm 13.5$</td>
<td>$2538.3 \pm 13.5$</td>
<td>$672.8 \pm 1.9$</td>
<td>$265.1 \pm 1.6$</td>
<td>$271.1 \pm 1.7$</td>
</tr>
</tbody>
</table>

$T = (298.174 \pm 0.058)$ K, $p = (20.3024 \pm 0.0031)$ MPa

$k_{\text{cell}} = (0.06478 \pm 0.00027)$ cm$^{-1}$

$\kappa_w^{\text{exp}} = (1.1976 \pm 0.0095) \cdot 10^{-6}$ S·cm$^{-1}$

$T = (374.216 \pm 0.075)$ K, $p = (21.2841 \pm 0.0037)$ MPa

$k_{\text{cell}} = (0.066914 \pm 0.000089)$ cm$^{-1}$

$\kappa_w^{\text{exp}} = (1.98 \pm 0.21) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$ (mol·kg$^{-1}$)</th>
<th>$c \cdot 10^6$ (mol·L$^{-1}$)</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$ (S·cm$^{-1}$)</th>
<th>$\Lambda^{\text{exp}}$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\Lambda^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl(aq)</td>
<td>$156.59 \pm 0.14$</td>
<td>$151.47 \pm 0.14$</td>
<td>$60.304 \pm 0.021$</td>
<td>$398.13 \pm 0.38$</td>
<td>$401.92 \pm 0.38$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4$ (aq)</td>
<td>$1061.8 \pm 6.4$</td>
<td>$1027.0 \pm 6.2$</td>
<td>$600.479 \pm 0.076$</td>
<td>$584.7 \pm 3.5$</td>
<td>$762.3 \pm 2.8$</td>
</tr>
<tr>
<td>KH$_2$PO$_4$ (aq)</td>
<td>$132.76 \pm 0.11$</td>
<td>$128.41 \pm 0.10$</td>
<td>$38.227 \pm 0.013$</td>
<td>$295.75 \pm 0.26$</td>
<td>$298.88 \pm 0.35$</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>$107.14 \pm 0.36$</td>
<td>$103.64 \pm 0.35$</td>
<td>$89.120 \pm 0.032$</td>
<td>$859.9 \pm 2.9$</td>
<td>$865.4 \pm 2.9$</td>
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<tr>
<td>KOH(aq)</td>
<td>$264.0 \pm 1.6$</td>
<td>$255.4 \pm 1.5$</td>
<td>$159.322 \pm 0.077$</td>
<td>$623.9 \pm 3.7$</td>
<td>$632.4 \pm 3.8$</td>
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Table 4.1. Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^\circ$</th>
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<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>156.59 ± 0.14</td>
<td>145.36 ± 0.13</td>
<td>84.212 ± 0.023</td>
<td>579.35 ± 0.54</td>
<td>585.40 ± 0.54</td>
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<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>1061.8 ± 6.4</td>
<td>985.6 ± 6.0</td>
<td>620.52 ± 0.71</td>
<td>629.6 ± 3.9</td>
<td>946.8 ± 3.5</td>
</tr>
<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>132.76 ± 0.11</td>
<td>123.230 ± 0.099</td>
<td>54.877 ± 0.015</td>
<td>443.71 ± 0.38</td>
<td>448.74 ± 0.52</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>107.14 ± 0.36</td>
<td>99.46 ± 0.33</td>
<td>107.052 ± 0.021</td>
<td>1076.4 ± 3.6</td>
<td>1083.4 ± 3.6</td>
</tr>
<tr>
<td>KOH(aq)*</td>
<td>[264.0 ± 1.6]</td>
<td>[245.1 ± 1.5]</td>
<td>[192.61 ± 0.12]</td>
<td>[785.9 ± 4.7]</td>
<td>[797.0 ± 4.8]</td>
</tr>
</tbody>
</table>

$T = (423.295 ± 0.048)$ K, $p = (21.3050 ± 0.0055)$ MPa
$k_{cell} = (0.066680 ± 0.000089)$ cm$^{-1}$
$\kappa_{w}^{exp} = (2.854 ± 0.033) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^\circ$</th>
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<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>495.27 ± 0.25</td>
<td>435.96 ± 0.22</td>
<td>318.85 ± 0.12</td>
<td>731.38 ± 0.46</td>
<td>750.23 ± 0.47</td>
</tr>
<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>3620.3 ± 19.9</td>
<td>3186.3 ± 17.5</td>
<td>1233.11 ± 0.57</td>
<td>387.0 ± 2.1</td>
<td>1019.6 ± 2.7</td>
</tr>
<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>692.17 ± 0.23</td>
<td>609.27 ± 0.20</td>
<td>336.998 ± 0.094</td>
<td>551.94 ± 0.24</td>
<td>567.78 ± 0.31</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>839.9 ± 2.1</td>
<td>739.5 ± 1.9</td>
<td>870.69 ± 0.12</td>
<td>1177.7 ± 3.0</td>
<td>1202.0 ± 3.0</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>1687.8 ± 9.1</td>
<td>1485.7 ± 8.0</td>
<td>1443.0 ± 1.0</td>
<td>971.3 ± 5.3</td>
<td>1005.1 ± 5.5</td>
</tr>
</tbody>
</table>

$T = (471.88 ± 0.10)$ K, $p = (21.2994 ± 0.0082)$ MPa
$k_{cell} = (0.0666847 ± 0.000089)$ cm$^{-1}$
$\kappa_{w}^{exp} = (3.654 ± 0.030) \cdot 10^{-6}$ S·cm$^{-1}$

---

153
Table 4.1.  Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>( m_{aq} \cdot 10^6 ) mol·kg(^{-1} )</th>
<th>( c \cdot 10^6 ) mol·L(^{-1} )</th>
<th>( \kappa_{corr} \cdot 10^6 ) S·cm(^{-1} )</th>
<th>( \Lambda^{\exp} ) S·cm(^2)·mol(^{-1} )</th>
<th>( \Lambda^\circ ) S·cm(^2)·mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl(aq)</td>
<td>747.52 ± 0.33</td>
<td>635.28 ± 0.28</td>
<td>525.96 ± 0.40</td>
<td>827.92 ± 0.73</td>
<td>853.61 ± 0.75</td>
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<tr>
<td>H(_3)PO(_4)(aq)</td>
<td>6136.1 ± 33.1</td>
<td>5213.5 ± 28.1</td>
<td>1435.3 ± 2.5</td>
<td>275.3 ± 1.6</td>
<td>1080.2 ± 4.0</td>
</tr>
<tr>
<td>KH(_2)PO(_4)(aq)</td>
<td>615.75 ± 0.22</td>
<td>523.29 ± 0.19</td>
<td>332.96 ± 0.24</td>
<td>635.17 ± 0.52</td>
<td>658.46 ± 0.59</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>748.1 ± 1.9</td>
<td>635.8 ± 1.6</td>
<td>794.5 ± 1.9</td>
<td>1249.7 ± 4.4</td>
<td>1275.4 ± 4.5</td>
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<tr>
<td>KOH(aq)</td>
<td>1338.9 ± 7.3</td>
<td>1137.9 ± 6.2</td>
<td>1250.9 ± 2.3</td>
<td>1099.3 ± 6.3</td>
<td>1133.1 ± 6.5</td>
</tr>
</tbody>
</table>

\( T = (498.02 ± 0.67) \) K, \( p = (21.073 ± 0.011) \) MPa
\( k_{cell} = (0.06563 ± 0.00015) \) cm\(^{-1} \)
\( \kappa_w^{\exp} = (3.823 ± 0.029) \cdot 10^{-6} \) S·cm\(^{-1} \)

<table>
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<tr>
<th>Solute</th>
<th>( m_{aq} \cdot 10^6 ) mol·kg(^{-1} )</th>
<th>( c \cdot 10^6 ) mol·L(^{-1} )</th>
<th>( \kappa_{corr} \cdot 10^6 ) S·cm(^{-1} )</th>
<th>( \Lambda^{\exp} ) S·cm(^2)·mol(^{-1} )</th>
<th>( \Lambda^\circ ) S·cm(^2)·mol(^{-1} )</th>
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</thead>
<tbody>
<tr>
<td>KCl(aq)</td>
<td>747.52 ± 0.33</td>
<td>610.46 ± 0.27</td>
<td>547.21 ± 0.54</td>
<td>896.39 ± 0.97</td>
<td>925.0 ± 1.0</td>
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<td>H(_3)PO(_4)(aq)</td>
<td>6136.1 ± 33.1</td>
<td>5009.8 ± 27.0</td>
<td>1153.51 ± 0.76</td>
<td>230.3 ± 1.3</td>
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<td>KH(_2)PO(_4)(aq)</td>
<td>615.75 ± 0.22</td>
<td>502.85 ± 0.18</td>
<td>351.17 ± 0.10</td>
<td>697.31 ± 0.33</td>
<td>723.21 ± 0.42</td>
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<tr>
<td>HCl(aq)</td>
<td>748.1 ± 1.9</td>
<td>611.0 ± 1.6</td>
<td>800.5 ± 1.5</td>
<td>1310.3 ± 4.2</td>
<td>1338.9 ± 4.3</td>
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<tr>
<td>KOH(aq)</td>
<td>1420.8 ± 7.7</td>
<td>1160.3 ± 6.3</td>
<td>1359.0 ± 2.5</td>
<td>1171.3 ± 6.7</td>
<td>1209.8 ± 6.9</td>
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</table>

\( T = (523.56 ± 0.44) \) K, \( p = (21.1355 ± 0.0042) \) MPa
\( k_{cell} = (0.06562 ± 0.00015) \) cm\(^{-1} \)
\( \kappa_w^{\exp} = (3.8906 ± 0.0059) \cdot 10^{-6} \) S·cm\(^{-1} \)
### Table 4.1. Continued

<table>
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<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^\circ$</th>
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</thead>
<tbody>
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<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td><strong>KCl(aq)</strong></td>
<td>582.37 ± 0.27</td>
<td>453.15 ± 0.21</td>
<td>439.14 ± 0.32</td>
<td>969.08 ± 0.83</td>
<td>997.39 ± 0.85</td>
</tr>
<tr>
<td><strong>H$_3$PO$_4$(aq)</strong></td>
<td>5735.3 ± 31.0</td>
<td>4461.7 ± 24.1</td>
<td>836.87 ± 0.27</td>
<td>187.6 ± 1.0</td>
<td>1149.2 ± 3.4</td>
</tr>
<tr>
<td><strong>KH$_2$PO$_4$(aq)</strong></td>
<td>728.59 ± 0.26</td>
<td>566.92 ± 0.20</td>
<td>423.95 ± 0.22</td>
<td>747.06 ± 0.47</td>
<td>778.35 ± 0.56</td>
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<tr>
<td><strong>HCl(aq)</strong></td>
<td>671.8 ± 1.7</td>
<td>522.7 ± 1.4</td>
<td>699.41 ± 0.59</td>
<td>1338.0 ± 3.6</td>
<td>1368.3 ± 3.7</td>
</tr>
<tr>
<td><strong>KOH(aq)</strong></td>
<td>1806.9 ± 9.7</td>
<td>1406.1 ± 7.6</td>
<td>1686.6 ± 3.2</td>
<td>1199.5 ± 6.8</td>
<td>1247.2 ± 7.1</td>
</tr>
</tbody>
</table>

$T = (548.63 ± 0.20)$ K, $p = (20.1351 ± 0.0058)$ MPa

$\kappa_{cell} = (0.06560 ± 0.00015)$ cm$^{-1}$

$\kappa_{w}^{exp} = (3.6382 ± 0.0049) \cdot 10^{-6}$ S·cm$^{-1}$

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<th>$\kappa_{corr} \cdot 10^6$</th>
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</tr>
<tr>
<td><strong>KCl(aq)</strong></td>
<td>582.37 ± 0.27</td>
<td>453.15 ± 0.21</td>
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<td>969.08 ± 0.83</td>
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</tr>
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<td>778.35 ± 0.56</td>
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<tr>
<td><strong>HCl(aq)</strong></td>
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<td>699.41 ± 0.59</td>
<td>1338.0 ± 3.6</td>
<td>1368.3 ± 3.7</td>
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<tr>
<td><strong>KOH(aq)</strong></td>
<td>1806.9 ± 9.7</td>
<td>1406.1 ± 7.6</td>
<td>1686.6 ± 3.2</td>
<td>1199.5 ± 6.8</td>
<td>1247.2 ± 7.1</td>
</tr>
</tbody>
</table>

$T = (571.91 ± 0.27)$ K, $p = (21.1465 ± 0.0052)$ MPa

$\kappa_{cell} = (0.06558 ± 0.00015)$ cm$^{-1}$

$\kappa_{w}^{exp} = (3.2953 ± 0.0034) \cdot 10^{-6}$ S·cm$^{-1}$

*KOH: solution at 423.295 K suspected of CO$_2$(g) contamination, affecting values of $m_{aq}$, $c$, $\kappa$, $\Lambda^{exp}$ and $\Lambda^\circ$
Table 4.2. Values of experimental molar conductivities, $\Lambda^{\text{exp}}$, and fitted limiting molar conductivities, $\Lambda^{\circ}$ for KCl(aq), D$_3$PO$_4$(aq), KD$_2$PO$_4$(aq), DCl(aq), and KOD(aq) in D$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa

<table>
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<tr>
<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^{\text{exp}}$</th>
<th>$\Lambda^{\circ}$</th>
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<td>mol·kg$^{-1}$</td>
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<td>S·cm$^2$·mol$^{-1}$</td>
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<tr>
<td>KCl(aq)</td>
<td>1116.43 ± 0.47</td>
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<td>1244.45 ± 0.47</td>
<td>150.09 ± 0.54</td>
<td>120.61 ± 0.44</td>
<td>123.29 ± 0.45</td>
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<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>6105.2 ± 11.5</td>
<td>6787.0 ± 11.5</td>
<td>6803.7 ± 11.6</td>
<td>989.5 ± 2.5</td>
<td>145.44 ± 0.45</td>
<td>273.9 ± 1.5</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>822.77 ± 0.37</td>
<td>914.66 ± 0.37</td>
<td>917.12 ± 0.37</td>
<td>79.318 ± 0.038</td>
<td>86.307 ± 0.054</td>
<td>88.350 ± 0.066</td>
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<tr>
<td>DCl(aq)</td>
<td>3244.1 ± 10.4</td>
<td>3606.5 ± 10.4</td>
<td>3616.0 ± 10.5</td>
<td>1090.9 ± 2.9</td>
<td>301.7 ± 1.2</td>
<td>308.8 ± 1.2</td>
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<tr>
<td>KOD(aq)</td>
<td>1108.8 ± 4.5</td>
<td>1232.6 ± 4.5</td>
<td>1235.9 ± 4.5</td>
<td>210.87 ± 0.70</td>
<td>170.61 ± 0.84</td>
<td>173.71 ± 0.86</td>
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</table>

$T = (298.174 ± 0.058)$ K, $p = (20.3024 ± 0.0031)$ MPa

$k_{\text{cell}} = (0.06478 ± 0.00027)$ cm$^{-1}$

$\kappa_{\text{exp}}^{\circ} = (1.6 ± 1.5) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
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<tr>
<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^{\text{exp}}$</th>
<th>$\Lambda^{\circ}$</th>
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<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>125.57 ± 0.13</td>
<td>139.59 ± 0.13</td>
<td>134.77 ± 0.13</td>
<td>46.031 ± 0.015</td>
<td>341.55 ± 0.34</td>
<td>344.62 ± 0.35</td>
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<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>823.4 ± 2.1</td>
<td>915.3 ± 2.1</td>
<td>883.7 ± 2.0</td>
<td>333.234 ± 0.028</td>
<td>377.09 ± 0.91</td>
<td>562.5 ± 2.2</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>108.82 ± 0.11</td>
<td>120.97 ± 0.11</td>
<td>116.79 ± 0.11</td>
<td>30.403 ± 0.014</td>
<td>257.52 ± 0.27</td>
<td>260.10 ± 0.36</td>
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<tr>
<td>DCl(aq)</td>
<td>1026.7 ± 3.5</td>
<td>1141.4 ± 3.5</td>
<td>1102.0 ± 3.4</td>
<td>694.4 ± 1.1</td>
<td>630.1 ± 2.2</td>
<td>647.0 ± 2.2</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>182.78 ± 0.83</td>
<td>203.20 ± 0.83</td>
<td>196.18 ± 0.80</td>
<td>77.255 ± 0.050</td>
<td>393.8 ± 1.6</td>
<td>397.7 ± 1.6</td>
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</table>

$T = (374.216 ± 0.075)$ K, $p = (21.2841 ± 0.0037)$ MPa

$k_{\text{cell}} = (0.066914 ± 0.000089)$ cm$^{-1}$

$\kappa_{\text{exp}}^{\circ} = (6.071 ± 0.065) \cdot 10^{-6}$ S·cm$^{-1}$
Table 4.2. Continued

<table>
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<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{\text{exp}}$</th>
<th>$\Lambda^{\circ}$</th>
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<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>125.57 ± 0.13</td>
<td>139.59 ± 0.13</td>
<td>129.32 ± 0.12</td>
<td>68.218 ± 0.026</td>
<td>527.52 ± 0.54</td>
<td>532.59 ± 0.54</td>
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<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>823.4 ± 2.1</td>
<td>915.3 ± 2.1</td>
<td>847.9 ± 1.9</td>
<td>344.30 ± 0.15</td>
<td>406.04 ± 0.94</td>
<td>721.2 ± 2.6</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>108.82 ± 0.11</td>
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<td>420.06 ± 0.46</td>
<td>424.37 ± 0.61</td>
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<tr>
<td>DCI(aq)</td>
<td>1026.7 ± 3.5</td>
<td>1141.4 ± 3.5</td>
<td>1057.4 ± 3.3</td>
<td>854.32 ± 0.33</td>
<td>807.9 ± 2.5</td>
<td>829.4 ± 2.6</td>
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<tr>
<td>KOD(aq)*</td>
<td>[182.78 ± 0.83]</td>
<td>[203.20 ± 0.83]</td>
<td>[188.25 ± 0.80]</td>
<td>[87.735 ± 0.080]</td>
<td>[466.1 ± 2.0]</td>
<td>[471.9 ± 2.0]</td>
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</table>

$T = (423.295 ± 0.048) \text{ K}, p = (21.3050 ± 0.0055) \text{ MPa}$

$k_{\text{cell}} = (0.066880 ± 0.000089) \text{ cm}^{-1}$

$\kappa_{\text{exp}}^{\circ} = (9.422 ± 0.031) \cdot 10^6 \text{ S·cm}^{-1}$

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<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
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<td>S·cm$^{-2}$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>824.56 ± 0.36</td>
<td>916.66 ± 0.36</td>
<td>804.62 ± 0.32</td>
<td>510.89 ± 0.42</td>
<td>634.95 ± 0.58</td>
<td>658.98 ± 0.60</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>4753.5 ± 9.0</td>
<td>5284.3 ± 9.0</td>
<td>4637.5 ± 7.9</td>
<td>911.73 ± 0.40</td>
<td>196.60 ± 0.35</td>
<td>828.7 ± 2.7</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>696.86 ± 0.34</td>
<td>774.68 ± 0.34</td>
<td>679.99 ± 0.30</td>
<td>340.24 ± 0.27</td>
<td>499.67 ± 0.45</td>
<td>514.57 ± 0.52</td>
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<tr>
<td>DCI(aq)</td>
<td>3010.1 ± 9.6</td>
<td>3346.2 ± 9.6</td>
<td>2937.2 ± 8.5</td>
<td>2729.9 ± 0.93</td>
<td>929.4 ± 2.7</td>
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<td>KOD(aq)</td>
<td>831.9 ± 3.4</td>
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<td>811.8 ± 3.0</td>
<td>613.59 ± 0.28</td>
<td>755.9 ± 2.8</td>
<td>780.0 ± 2.9</td>
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Table 4.2.  Continued

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<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>609.67 ± 0.28</td>
<td>677.76 ± 0.28</td>
<td>573.98 ± 0.24</td>
<td>414.63 ± 0.32</td>
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<td>745.67 ± 0.65</td>
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<td>D$_3$PO$_4$(aq)</td>
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<td>5324.4 ± 8.9</td>
<td>838.68 ± 0.27</td>
<td>157.52 ± 0.27</td>
<td>903.6 ± 5.6</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>565.92 ± 0.27</td>
<td>629.13 ± 0.27</td>
<td>532.78 ± 0.23</td>
<td>307.93 ± 0.16</td>
<td>577.46 ± 0.40</td>
<td>593.58 ± 0.48</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>2283.6 ± 7.4</td>
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<td>2177.2 ± 11.5</td>
<td>1012.7 ± 6.1</td>
<td>1055.7 ± 6.4</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>661.6 ± 2.7</td>
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<td>622.9 ± 2.3</td>
<td>563.86 ± 0.82</td>
<td>905.3 ± 3.6</td>
<td>929.5 ± 3.7</td>
</tr>
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</table>

$T$ = (498.02 ± 0.67) K, $p$ = (21.073 ± 0.011) MPa

$k_{cell} = (0.06563 ± 0.00015) \text{ cm}^{-1}$

$\kappa_{w}^{\exp} = (3.097 ± 0.068) \cdot 10^{-6} \text{ S·cm}^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m \cdot 10^6$</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{\exp}$</th>
<th>$\Lambda^{\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>609.67 ± 0.28</td>
<td>677.76 ± 0.28</td>
<td>551.08 ± 0.23</td>
<td>437.17 ± 0.38</td>
<td>793.29 ± 0.76</td>
<td>819.25 ± 0.79</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>5657.0 ± 10.5</td>
<td>6288.7 ± 10.5</td>
<td>5112.0 ± 8.6</td>
<td>675.82 ± 0.17</td>
<td>132.20 ± 0.22</td>
<td>962.5 ± 3.9</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>565.92 ± 0.27</td>
<td>629.13 ± 0.27</td>
<td>511.53 ± 0.22</td>
<td>329.152 ± 0.084</td>
<td>643.41 ± 0.33</td>
<td>668.34 ± 0.45</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>2283.6 ± 7.4</td>
<td>2538.7 ± 7.4</td>
<td>2064.2 ± 6.0</td>
<td>2200.0 ± 5.6</td>
<td>1065.8 ± 4.1</td>
<td>1113.4 ± 4.3</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>715.9 ± 2.9</td>
<td>795.9 ± 2.9</td>
<td>647.1 ± 2.4</td>
<td>631.19 ± 0.66</td>
<td>975.4 ± 3.7</td>
<td>1003.4 ± 3.8</td>
</tr>
</tbody>
</table>

$T$ = (523.56 ± 0.44) K, $p$ = (21.1355 ± 0.0042) MPa

$k_{cell} = (0.06562 ± 0.00015) \text{ cm}^{-1}$

$\kappa_{w}^{\exp} = (3.072 ± 0.072) \cdot 10^{-6} \text{ S·cm}^{-1}$
<table>
<thead>
<tr>
<th>Solute</th>
<th>(m \cdot 10^6)</th>
<th>(m_{aq} \cdot 10^6)</th>
<th>(c \cdot 10^6)</th>
<th>(\kappa_{corr} \cdot 10^6)</th>
<th>(\Lambda^{exp})</th>
<th>(\Lambda^o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg(^{-1})</td>
<td>mol·kg(^{-1})</td>
<td>mol·L(^{-1})</td>
<td>S·cm(^{-1})</td>
<td>S·cm(^2)·mol(^{-1})</td>
<td>S·cm(^2)·mol(^{-1})</td>
</tr>
<tr>
<td>T = (548.63 ± 0.20) K, (p = (20.1351 ± 0.0058)) MPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{cell})</td>
<td>0.06560 ± 0.00015 cm(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\kappa_w^{exp})</td>
<td>(2.990 ± 0.010)·10(^{-6}) S·cm(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>681.09 ± 0.34</td>
<td>757.16 ± 0.34</td>
<td>585.93 ± 0.26</td>
<td>506.43 ± 0.30</td>
<td>864.31 ± 0.64</td>
<td>894.92 ± 0.67</td>
</tr>
<tr>
<td>D(_3)PO(_4)(aq)</td>
<td>3841.6 ± 7.4</td>
<td>4270.7 ± 7.4</td>
<td>3304.3 ± 5.7</td>
<td>418.556 ± 0.076</td>
<td>126.67 ± 0.22</td>
<td>976.4 ± 3.4</td>
</tr>
<tr>
<td>KD(_2)PO(_4)(aq)</td>
<td>501.72 ± 0.25</td>
<td>557.75 ± 0.25</td>
<td>431.62 ± 0.19</td>
<td>303.552 ± 0.092</td>
<td>704.02 ± 0.38</td>
<td>730.34 ± 0.51</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>2405.8 ± 7.8</td>
<td>2674.4 ± 7.8</td>
<td>2069.7 ± 6.1</td>
<td>2249.8 ± 3.7</td>
<td>1087.0 ± 3.7</td>
<td>1141.0 ± 3.9</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>958.7 ± 3.9</td>
<td>1065.7 ± 3.9</td>
<td>824.73 ± 3.0</td>
<td>839.50 ± 0.91</td>
<td>1017.9 ± 3.9</td>
<td>1053.8 ± 4.0</td>
</tr>
<tr>
<td>T = (571.91 ± 0.27) K, (p = (21.1465 ± 0.0052)) MPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{cell})</td>
<td>0.06558 ± 0.00015 cm(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\kappa_w^{exp})</td>
<td>(3.062 ± 0.080)·10(^{-6}) S·cm(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>681.09 ± 0.34</td>
<td>757.16 ± 0.34</td>
<td>555.70 ± 0.25</td>
<td>518.58 ± 0.67</td>
<td>933.2 ± 1.3</td>
<td>967.2 ± 1.3</td>
</tr>
<tr>
<td>D(_3)PO(_4)(aq)</td>
<td>3841.6 ± 7.4</td>
<td>4270.7 ± 7.4</td>
<td>3133.7 ± 5.4</td>
<td>318.75 ± 0.12</td>
<td>101.72 ± 0.18</td>
<td>1023.5 ± 4.2</td>
</tr>
<tr>
<td>KD(_2)PO(_4)(aq)</td>
<td>501.72 ± 0.25</td>
<td>557.75 ± 0.25</td>
<td>409.34 ± 0.18</td>
<td>316.40 ± 0.39</td>
<td>774.3 ± 1.0</td>
<td>803.6 ± 1.1</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>2405.8 ± 7.8</td>
<td>2674.4 ± 7.8</td>
<td>1963.0 ± 5.7</td>
<td>2213.7 ± 4.7</td>
<td>1127.7 ± 4.1</td>
<td>1187.1 ± 4.3</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>649.11 ± 2.7</td>
<td>721.6 ± 2.7</td>
<td>529.6 ± 2.0</td>
<td>583.58 ± 0.23</td>
<td>1101.9 ± 4.1</td>
<td>1135.2 ± 4.3</td>
</tr>
</tbody>
</table>

*KOD: solution at 423.295 K suspected of CO\(_2\)(g) contamination, affecting values of \(m_{aq}, c, \kappa, \Lambda^{exp}\) and \(\Lambda^o\)*
\[ \text{H}_2\text{O} \xrightleftharpoons{} \text{H}^+ + \text{OH}^- \]  
(4.16)

\[ m_{\text{aq,OH}^-} = \frac{K_w}{m_{\text{aq,H}^+}} \]  
(4.17)

Through mass balance:

\[ m_{\text{aq,H}_3\text{PO}_4} + m_{\text{aq,H}^+} = m_{\text{aq,(HPO}_4^{2-})} + m_{\text{aq,OH}^-} \]  
(4.18)

Therefore:

\[ m_{\text{aq,H}^+} = \frac{K_{2a} \cdot m_{\text{aq,H}_2\text{PO}_4^-} + K_w}{\sqrt{\left(\frac{m_{\text{aq,H}_2\text{PO}_4^-}}{K_{1a}}\right) + 1}} \]  
(4.19)

Values of \( m_{\text{aq,H}^+} \) are entered into equations (4.14) and (4.15) to calculate \( m_{\text{aq,H}_3\text{PO}_4} \) and \( m_{\text{aq,(HPO}_4^{2-})} \), respectively.

The degree of hydrolysis of \( \text{H}_2\text{PO}_4^- \), \( \alpha_2 \), was estimated from the first ionization constant of phosphoric acid, which was calculated from the HKF model reported by Shock and Helgeson (1990), using the SUPCRT92 software (Johnson et al., 1992). Using the inverse of the first ionization constant, \( K_{1a} \), the amount of \( \text{H}_3\text{PO}_4 \) that arises from the hydrolysis equilibrium reaction was estimated for each set of measurements, and converted to values of \( c \) (\( c_{\alpha_2} \)) and \( m_{\text{aq}} \) (\( m_{\text{aq,\alpha_2}} \)). Corrected values of concentration \( (c_{\text{eq}} = c - c_{\alpha_2}) \) and aquamolality \( (m_{\text{aq,eq}} = m_{\text{aq}} - m_{\text{aq,\alpha_2}}) \) were then calculated. Using the SUPCRT92 software, the second ionization constant of phosphoric acid, \( K_{2a} \), was used to estimate the degree of dissociation of \( \text{H}_2\text{PO}_4^- \), \( \beta \). The amount of \( \text{HPO}_4^{2-} \) created from the ionization of \( \text{H}_3\text{PO}_4^- \) was estimated for each set of measurements, and converted to values of \( c \) (\( c_{\beta_2} \)) and \( m_{\text{aq}} \) (\( m_{\text{aq,\beta}_2} \)). New, corrected values of concentration \( (c_{\text{eq}} = c - c_{\beta_2} - c_{\alpha_2}) \) and aquamolality \( (m_{\text{aq,eq}} = m_{\text{aq}} - m_{\text{aq,\beta}_2} - m_{\text{aq,\alpha_2}}) \) were then calculated for \( \text{H}_2\text{PO}_4^- \) in solution.
We also corrected the experimentally measured values of conductivity of \( \text{H}_2\text{PO}_4^- \), according to reaction (4.13). We used reported values of \( \Lambda_{\text{exp}}^{\text{H}_2\text{PO}_4} \) for \( \text{K}_2\text{HPO}_4 \) from Mucitelli and DiAngelo (1994) to estimate the value of \( \lambda_{(\text{HPO}_4)^2^-} \), by assuming that values of \( \lambda_{K^+}^{\circ} \), reported by Marshall (1987b), were approximately equal to \( \lambda_{K^+} \). Estimated values of \( \lambda_{(\text{HPO}_4)^2^-} \) were used to calculate values of \( \kappa_{(\text{HPO}_4)^2^-} \), which were subtracted from experimental values of \( \kappa \) for \( \text{H}_2\text{PO}_4^- \) to obtain corrected values of \( \kappa \) for \( \text{H}_2\text{PO}_4^- \) \( (\kappa_{\text{eq}} = \kappa - \kappa_{(\text{HPO}_4)^2^-}) \). Using the final corrected values of \( c_{\text{eq}} \) and \( \kappa_{\text{eq}} \) for \( \text{KH}_2\text{PO}_4 \), corrected values of \( \Lambda_{\text{exp}} (\Lambda_{\text{exp,eq}} = \kappa_{\text{eq}}/c_{\text{eq}}) \) for \( \text{KH}_2\text{PO}_4 \) were then calculated. The extent of the corresponding amphiprotic effects of \( \text{D}_2\text{PO}_4^- \) in \( \text{D}_2\text{O} \) were estimated by assuming that the values of the \( K_{1\alpha} \) and \( K_{2\alpha} \) of phosphoric acid in \( \text{D}_2\text{O} \) were identical to that in \( \text{H}_2\text{O} \), on an aquamolality scale. Values of the calculated degree of ionization of \( \text{H}_2\text{PO}_4^- \), \( \beta_2 \), hydrolysis of \( \text{H}_2\text{PO}_4^- \), \( \alpha_2 \), total amphiprotic ionization, \( \beta_2 + \alpha_2 \), at each temperature, and the corrected values of \( \Lambda_{\text{exp,eq}} \) and \( m_{\text{aq,eq}} \) for \( \text{KH}_2\text{PO}_4 \) and \( \text{KD}_2\text{PO}_4 \) are listed in the Appendix, Tables E.7 and E.8. In all cases, the correction was less than 2.5 percent. Equation (4.11) was then used, as described above, to determine the limiting molar conductivities, \( \Lambda^{\circ} \), of \( \text{KH}_2\text{PO}_4 \): 
\[
\Lambda_{\text{KH}_2\text{PO}_4}^{\circ} = [\lambda_{K^+}^{\circ} + \lambda_{\text{H}_2\text{PO}_4}^{\circ}] ,
\]
and \( \text{KD}_2\text{PO}_4 \): 
\[
\Lambda_{\text{KD}_2\text{PO}_4}^{\circ} = [\lambda_{K^+}^{\circ} + \lambda_{\text{D}_2\text{PO}_4}^{\circ}] .
\]
The values of \( \Lambda^{\circ} \) for each acid and electrolyte in \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), derived from this fitting procedure, are tabulated in Tables 4.1 and 4.2.

### 4.4.2 Values of \( pK_{aq} \) and \( \Delta pK_{aq} \)

Table 4.3 reports the experimental values of the first ionization constant of phosphoric acid in both \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \). Although, the values calculated from these experimental conductance results, using equation (4.5), are expressed in terms of the
Table 4.3. Calculated values of $K_{aq}$, $pK_{aq}$ and $\Delta pK_{aq}$ for H$_3$PO$_4$ and D$_3$PO$_4$ from $T = 298$ K to $T = 571$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$K_{aq} \times 10^4$</th>
<th>H$_3$PO$_4$</th>
<th>D$_3$PO$_4$</th>
<th>$pK_{aq}$ H$_3$PO$_4$</th>
<th>$pK_{aq}$ D$_3$PO$_4$</th>
<th>$\Delta pK_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.174 ± 0.058</td>
<td>20.3024 ± 0.0031</td>
<td>89.50 ± 0.68</td>
<td>38.67 ± 0.24</td>
<td>2.0482 ± 0.0033</td>
<td>2.4126 ± 0.0027</td>
<td>0.3645 ± 0.0042</td>
<td></td>
</tr>
<tr>
<td>374.216 ± 0.075</td>
<td>21.2841 ± 0.0036</td>
<td>26.99 ± 0.19</td>
<td>12.390 ± 0.057</td>
<td>2.5688 ± 0.0031</td>
<td>2.9071 ± 0.0020</td>
<td>0.3383 ± 0.0037</td>
<td></td>
</tr>
<tr>
<td>423.295 ± 0.048</td>
<td>21.3050 ± 0.0055</td>
<td>13.860 ± 0.099</td>
<td>6.520 ± 0.028</td>
<td>2.8584 ± 0.0031</td>
<td>3.1855 ± 0.0018</td>
<td>0.3271 ± 0.0036</td>
<td></td>
</tr>
<tr>
<td>471.88 ± 0.10</td>
<td>21.2994 ± 0.0082</td>
<td>7.980 ± 0.049</td>
<td>3.690 ± 0.013</td>
<td>3.0978 ± 0.0027</td>
<td>3.4333 ± 0.0016</td>
<td>0.3355 ± 0.0031</td>
<td></td>
</tr>
<tr>
<td>498.02 ± 0.67</td>
<td>21.073 ± 0.011</td>
<td>4.990 ± 0.034</td>
<td>2.180 ± 0.014</td>
<td>3.3016 ± 0.0029</td>
<td>3.6618 ± 0.0028</td>
<td>0.3602 ± 0.0040</td>
<td></td>
</tr>
<tr>
<td>523.56 ± 0.44</td>
<td>21.1355 ± 0.0042</td>
<td>2.940 ± 0.019</td>
<td>1.2900 ± 0.0057</td>
<td>3.5319 ± 0.0028</td>
<td>3.8881 ± 0.0019</td>
<td>0.3562 ± 0.0034</td>
<td></td>
</tr>
<tr>
<td>548.63 ± 0.20</td>
<td>20.1351 ± 0.0058</td>
<td>1.700 ± 0.011</td>
<td>0.7800 ± 0.0031</td>
<td>3.7692 ± 0.0027</td>
<td>4.1069 ± 0.0017</td>
<td>0.3377 ± 0.0032</td>
<td></td>
</tr>
<tr>
<td>571.91 ± 0.27</td>
<td>21.1465 ± 0.0052</td>
<td>0.9000 ± 0.0056</td>
<td>0.4400 ± 0.0020</td>
<td>4.0478 ± 0.0027</td>
<td>4.3536 ± 0.0019</td>
<td>0.3058 ± 0.0034</td>
<td></td>
</tr>
</tbody>
</table>
hypothetical 1 molar standard state, $K_c$, we have chosen to report these results in terms of the aquamolal standard state, $K_{aq}$. Uncertainties were calculated as the root mean sum of squares, which is discussed in Appendix D.

4.5 Discussion

4.5.1 Comparison of Values of $\Lambda^\circ$

The experimental values for $\log[\Lambda^\circ]$, from Tables 4.1 and 4.2, are plotted in Figures 4.1 and 4.2 as a function of $\log[\eta_w]$, where $\eta_w$ is the viscosity of the solvent, in P. All of the experimental values of $\Lambda^\circ$ consistently increase with temperature in both solvents, as expected from the Stokes Einstein equation, and the sequence of values for each solute at each temperature is the same. However, the magnitudes of $\Lambda_{\text{KCl}}^\circ$, $\Lambda_{\text{HCl}}^\circ$, $\Lambda_{\text{KH}_2\text{PO}_4}^\circ$ and $\Lambda_{\text{KOH}}^\circ$ are greater in light water than the corresponding values in heavy water.

The experimental values for $\Lambda^\circ$ were fit to equation (1.45) (Zimmerman et al., 2012a, 2012b):

$$\log[\Lambda^\circ] = \log[A_1] + \left[A_2 + \frac{A_3}{\rho_w}\right] \cdot \log[\eta_w]$$  \hspace{1cm} (4.20)

$A_1$, $A_2$, and $A_3$ are all adjustable parameters. For each species in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, equation (4.20) was fitted to the temperature- and pressure-dependent experimental values of $\Lambda^\circ$, reported in Tables 4.1 and 4.2. The results are plotted in Figures 4.1 and 4.2, and tabulated in Table 4.4. Solutions of KOH and KOD at 423.295 K were not injected through the conductivity cell shortly after preparation (less than 72 hours), like all other solutions of KOH and KOD were. The KOH and KOD solutions remained in their
Figure 4.1. Plots of log[Λ°] as a function of log[η_{H2O}]: (■) KCl; (◇) KH$_2$PO$_4$; (▲) HCl; and (◇) KOH in H$_2$O. The solid lines represent fits to equation (4.20).
Figure 4.2. Plots of log[$\Lambda^o$] as a function of log[$\eta_{D_2O}$]: (■) KCl; (◇) KD$_2$PO$_4$; (▲) DCl; and (◇) KOD in D$_2$O. The solid lines represent fits to equation (4.20)
Table 4.4. Fitted parameters for the temperature dependence of limiting molar conductivities, $\Lambda^\circ$, of KCl, KH$_2$PO$_4$/KD$_2$PO$_4$, HCl/DCl and KOH/KOD in H$_2$O and D$_2$O, according to equation (4.20)****

<table>
<thead>
<tr>
<th>Solute:</th>
<th>H$_2$O</th>
<th>D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1^*$</td>
<td>$A_2^*$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>2.22 ± 0.16</td>
<td>-0.914 ± 0.022</td>
</tr>
<tr>
<td>KH$_2$PO$_4$/KD$_2$PO$_4$(aq)</td>
<td>1.356 ± 0.061</td>
<td>-0.9211 ± 0.0070</td>
</tr>
<tr>
<td>HCl/DCl(aq)</td>
<td>23.8 ± 2.7</td>
<td>-0.696 ± 0.036</td>
</tr>
<tr>
<td>KOH/KOD(aq)***</td>
<td>8.06 ± 0.79</td>
<td>-0.788 ± 0.033</td>
</tr>
</tbody>
</table>

*Both $A_1$ and $A_2$ are unit-less coefficients

**$A_3$ has units of cm$^3$·g$^{-1}$

***KOH and KOD: solutions at 423.295 K suspected of CO$_2$(g) contamination, therefore values of $\Lambda^\circ$ for KOH/KOD at 423.295 K were not included in the fitting procedure

****Uncertainty estimates are standard errors in the fitted coefficients
respective sealed pyrex® bottles for approximately 13 days under Ar(g). Therefore, we suspect these solutions may have been contaminated by CO$_2$(g), as a result of slow Ar(g) leaking from the bottles over time, thus affecting their values of $m_{aq}$, $c$, $\kappa$, $\Lambda^{\text{exp}}$ and $\Lambda^\circ$. Therefore, values of $\Lambda^\circ$ obtained from these solutions were not included in the fitting procedure of equation (4.20) or reported in any of the Figures.

The limiting molar conductivities from this study in H$_2$O are compared with those of previous workers in Figure 4.3, which plots the relative deviation of our experimental values of $\Lambda^\circ$ in light water, with those obtained from literature sources. These sources consisted of experimental values of $\Lambda^\circ$ reported by Ho et al. (2000a, 2000b, 2001) for KCl, HCl and KOH, all at temperatures greater than 373.15 K. At 298.15 K, values of $\Lambda^\circ$ for HCl and KOH reported by Tada et al. (1992, 1993) were used for comparison, and the value of $\Lambda^\circ$ for KCl reported by Ho et al. (2000a) was taken as the literature source. Values of $\Lambda^\circ$ for KH$_2$PO$_4$ reported by Mucitelli and DiAngleo (1994) were used for comparison purposes. It was found that Mucitelli and Diangelo did not account for the solvent correction in $\kappa$ shown in equation (2.6), which caused values of $\Lambda$ at 298 K for KH$_2$PO$_4$ at low concentration ($c \approx 1 \cdot 10^{-3}$ mol·L$^{-1}$) to deviate quite significantly from other literature sources (Mason and Culvern, 1949; Tsurko et al., 1999). Therefore, a comparison value of $\Lambda^\circ$ for KH$_2$PO$_4$ at 298.15 K was estimated using the value reported by Mason and Culvern (1949). In order to do a direct comparison of the values of $\Lambda^\circ$ reported in this thesis to those reported in the literature, literature values of log[$\Lambda^\circ$] for HCl, KCl, KOH and KH$_2$PO$_4$ were plotted as a function of log[$\eta_{H2O}$], according to equation (3.13):

$$\log[\Lambda^\circ] = a_L \cdot (\log[\eta_{H2O}])^2 + b_L \cdot \log[\eta_{H2O}] + c_L$$  

(4.21)
Figure 4.3. Comparison of experimental (exp.) and literature (lit.) values of $\Lambda^\circ$ as a function of $T$, as a relative % difference, for each solution: (■) KCl; (◇) KH$_2$PO$_4$; (▲) HCl; and (○) KOH in H$_2$O.
Literature values of $\Lambda^\circ$ for each of HCl, NaCl, NaOH and NaAc were then calculated at the same values of $\eta_{H2O}$ (which corresponded to the experimental values of $T$ and $p$) reported in this thesis. Calculated values of $a$, $b$ and $c$ are reported below in Table 4.5. The experimental values of $\Lambda^\circ$ for the species in H$_2$O in Table 4.1 deviate from the literature results by no more than seven percent and, in approximately one quarter of the cases, by less than five percent. These differences may reflect systematic errors in the cell constant which can arise from small changes in the dimensions of the cell over time, and our assumption that the theoretical expressions for $J_1$ and $J_2$ in the FHFP equation are accurate over our experimental range of concentrations. The agreement is therefore quite acceptable. Since almost all of our experimental values of $\Lambda^\circ$ for HCl, KCl, KOH and KH$_2$PO$_4$ are more positive than the literature values, there is a partial cancellation of systematic errors that occurs when using our values of $\Lambda^\circ$ in equation (4.10) to calculate $[\lambda_{H^+}^\circ + \lambda_{H2PO4}^\circ]$. This was our purpose in adopting the experimental design described above. Similar comparisons were done for the pertinent species in D$_2$O, at 298.15 K (the only known literature data available), Figure 4.4. These sources consisted of experimental values of $\Lambda^\circ$ reported by Swain and Evans (1966) for KCl and values of $\Lambda^\circ$ reported by Tada et al. (1992, 1993) for DCl and KOD. The experimental values of $\Lambda^\circ$ for the species in D$_2$O in Table 4.2 deviate from the literature results by no more than three percent. This indicates, at least at 298 K, that the experimental measurements of $\Lambda^\circ$ reported in this thesis for KCl, DCl and KOD in D$_2$O are consistent with the known literature data.
Table 4.5. Parameters used in equation (4.21) to calculate the limiting molar conductivities, $\Lambda^\circ$, from literature values of $\Lambda^\circ$ of KCl, KH$_2$PO$_4$, HCl and KOH, in H$_2$O, at the same values of $\eta_{\text{H}_2\text{O}}$ reported in this thesis

<table>
<thead>
<tr>
<th>Solute:</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_L^*$</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>-0.0391</td>
</tr>
<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>0.0517</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>-0.1441</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>-0.1536</td>
</tr>
</tbody>
</table>

*Coefficients $a_L$, $b_L$ and $c_L$ are unit-less
Figure 4.4. Comparison of experimental (exp.) and literature (lit.) values of $\Lambda^o$ at 298 K, as a relative % difference, for each solution: (■) KCl; (▲) DCl; and (○) KOD in D$_2$O.
4.5.2 Values of $pK_{aq}$ in H$_2$O

Figures 4.5 and 4.6 plot the experimental values of $pK_{aq}$ for phosphoric acid in H$_2$O, as represented by equation (4.2), at elevated temperatures, along with other values reported in the literature. Read (1988) and Tsurko et al. (1999) both used conductance methods similar to the one presented here to determine values of $pK_{aq}$. Rudolph (2010) used Raman spectroscopy. Paabo and Bates (1970) measured values of $pK_{aq}$ using potentiometry and Mesmer and Baes (1974) measured values of $pK_{aq,OH}$ for phosphoric acid using potentiometry:

$$H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O \quad (4.22)$$

These values were combined with values for the ionization of water from Marshall and Franck (1981), which were also measured using potentiometry, to calculate values of $pK_{aq}$ for phosphoric acid. As shown in Figures 4.5 and 4.6, the experimental values of $pK_{aq}$ correlate well with those previously reported in the literature at low temperatures, but deviate from those calculated using the values reported by Mesmer and Baes (1974) at higher temperatures. Read (1988) has noted a similar deviation, which he attributes to the potential presence of polyphosphates, however Mesmer and Baes were unable to detect the formation of any polyphosphates in their potentiometric studies. The results presented here coincide well with those of Read (1988) at all measured temperatures. It is important to note that values of $pK_{aq}$ calculated from potentiometry measurements are consistently higher, by approximately 0.05 units, when compared to those values of $pK_{aq}$ calculated from conductivity measurements, the exception being the values reported by Tsurko et al. (1999). This trend is seen in Figure 4.5, and more easily seen in Figure 4.6, the expanded version.
Figure 4.5. Experimental values for the first ionization constant of phosphoric acid in H$_2$O, pK$_{aq\text{H}_3\text{PO}_4}$ vs. $T$: (●) This work; (○) Marshall and Franck (1981) and Mesmer and Baes (1974); (◇) Read (1988); (X) Paabo and Bates (1970); (△) Tsurko et al. (1999) and (▽) Rudolph (2010). The solid curve is the fit of the density model, equation (4.24), to the data from Read (1988), Tsurko et al. (1999) and this work, Table 4.6.
Figure 4.6. Expanded version of the experimental values for the first ionization constant of phosphoric acid in H$_2$O from Figure 4.5, pK$_{aq,H_3PO_4}$ vs. $T$: (●) This work; (⊙) Marshall and Franck (1981) and Mesmer and Baes (1974); (○) Read (1988); (X) Paabo and Bates (1970); (△) Tsurko et al. (1999) and (▽) Rudolph (2010). The solid curve is the fit to the density model, equation (4.24).
As done by Bulemela and Tremaine (2009), we chose to model the temperature and pressure dependence of values of $pK_{aq}$ reported in this study and from Read (1988) and Tsurko et al. (1999), using the density model, reported by Mesmer et al. (1988), which relates the limiting high temperature behavior of equilibrium constants to the density of water, equations (1.19) and (1.20):

$$\log[K_{aq}] = \frac{a_d}{T} + \frac{b_d}{T^2} + \frac{c_d}{T^3} + \left[ e_d + \frac{f_d}{T} + \frac{g_d}{T^2} \right] \cdot \log[\rho_{H_2O}]$$  \hspace{1cm} (4.23)

Here, the constants $a_d$ through $g_d$ are adjustable fitting parameters, and $\rho_{H_2O}$ is the density of water at the temperature and pressure of interest, taken from Wagner and Prüß (2002). Adjustable parameters $d_d, f_d$ and $g_d$ were found to be statistically insignificant when modelling the values of $pK_{aq}$ using equation (4.23) in this study, and were therefore fixed to zero. The value of $pK_{aq}(298.15)$, reported by Mesmer and Baes (1974) and Marshall and Franck (1981), was found to be within the experimental error of the value of $pK_{aq}(298.15)$ reported by Tsurko et al. (1999), and reasonably close to the value reported by Read (1988). It was therefore used to fix the value of $a$ in equation (4.23). The corresponding version of equation (4.23) used in our calculations is as follows:

$$\log[K_{aq}] - \log[K_{aq}(298.15)] = b_d \cdot \left( \frac{1}{T} - \frac{1}{298.15} \right)$$

$$+ c_d \cdot \left( \frac{1}{T^2} - \frac{1}{298.15^2} \right) + [e_d] \cdot (\log[\rho_{H_2O}] - \log[\rho_{H_2O,298.15}])$$  \hspace{1cm} (4.24)

The fitted parameters are tabulated in Table 4.6, and the fit is plotted in Figures 4.5 and 4.6. The deviations between the fitted values of $pK_{aq}$ with our experimental values are plotted in Figure 4.7. In no case was the deviation between our experimental values of $pK_{aq}$ and those predicted by equation (4.24) greater than ± 0.05.
Table 4.6. Fitted parameters obtained for the ionization constant of phosphoric acid in H$_2$O and D$_2$O as a function of temperature and solvent density, equations (4.24) and (4.26)

<table>
<thead>
<tr>
<th>Parameter:</th>
<th>log $K_{aq}$</th>
<th></th>
<th>Parameter:</th>
<th>∆log $K_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_3$PO$_4$</td>
<td>D$_3$PO$_4^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_d$</td>
<td>-2.154***</td>
<td>-2.519***</td>
<td>$\Delta a_d$</td>
<td>-0.365***</td>
</tr>
<tr>
<td>$b_d \cdot 10^3$ / (K)</td>
<td>-0.681 ± 0.503</td>
<td>0.359 ± 0.602</td>
<td>$\Delta b_d \cdot 10^3$ / (K)</td>
<td>1.040 ± 0.356</td>
</tr>
<tr>
<td>$c_d \cdot 10^5$ / (K$^2$)</td>
<td>1.696 ± 0.810</td>
<td>-0.0340 ± 0.974</td>
<td>$\Delta c_d \cdot 10^5$ / (K$^2$)</td>
<td>-1.730 ± 0.540</td>
</tr>
<tr>
<td>$e_d$</td>
<td>12.403 ± 1.193</td>
<td>10.158 ± 1.390</td>
<td>$\Delta e_d$</td>
<td>-2.245 ± 0.713</td>
</tr>
</tbody>
</table>

Relative Standard Error 0.0237 0.0265 Relative Standard Error 0.0118

*Calculated from p$K_{aq,H3PO4}$ + ∆p$K_{aq}$ parameters. The standard uncertainty for log$K_{aq}(H_3PO_4)$ is calculated from the sum of the variances for log$K_{aq}(H_3PO_4)$ and ∆log$K_{aq}$

**Parameters $\Delta b_d$, $\Delta c_d$ and $\Delta e_d$ are those determined using equation (4.26) for ∆p$K_{aq}$

***The value of $a_d$ is calculated from equation (4.24) by setting $T = 298.15$ and fixing p$K_{aq}(298.15)$ to the calculated literature value from Marshall and Franck (1981) and Mesmer and Baes (1974), the value of $\Delta a$ is calculated from equation (4.26), by setting $T = 298.174$ and fixing p$K_{aq}(298.174)$ to the value reported in Table 4.3
Figure 4.7. Deviations between the experimental values and fitted "density" model for the first ionization constant of phosphoric acid in H$_2$O, \([pK_{aq,H_3PO_4}^{exp} - pK_{aq,H_3PO_4}^{pred}]\) vs. \(T\)
4.5.3 Values of $\Delta pK_{aq}$

The experimental values of $pK_{aq}$ for $H_3PO_4$ and $D_3PO_4$, reported in Table 4.3, are plotted in Figure 4.8 over the temperature range $T = 298$ K to $T = 571$ K, along with the experimental uncertainties. Experimental values of $\Delta pK_{aq} = [pK_{aq,D3PO4} - pK_{aq,H3PO4}]$ are plotted in Figures 4.9 and 4.10. As noted in Chapter 2, the experiments were designed to measure the difference in molar conductivity between solutions in $D_2O$ and $H_2O$ directly, so that most systematic errors would cancel. To maintain consistency with this approach, we chose to model the experimental values for $\Delta pK_{aq}$ directly, relative to the “density model” used for the light water data, equation (4.24). Following Bulemela and Tremaine (2009), we used the approximation $\rho_{D2O} \approx \rho_{H2O} (M_{D2O}/M_{H2O})$ to yield the corresponding expression for $\Delta pK_{aq}$ ($\Delta pK_{aq} = -\Delta \log[K_{aq}]$):

$$\Delta \log[K_{aq}] = \Delta a + \frac{\Delta b}{T} + \frac{\Delta c}{T^2} + \Delta e \cdot \log[\rho_{H2O}] + e \cdot \log\left[\frac{M_{D2O}}{M_{H2O}}\right],$$  \hspace{1cm} (4.25)

where $M_{H2O}$ and $M_{D2O}$ are the molar masses of $H_2O$ and $D_2O$, respectively. We chose to fix the value of $\Delta a$ in equation (4.25) with a value of $\Delta pK_{aq}$ at 298.174 K. There are only three known literature values of $pK_{aq,D3PO4}$: those measured by Paabo and Bates (1970) using potentiometry, from $T = 278$ K to $T = 323$ K; the value measured by McDougall and Long (1962) using conductivity, at 298 K; and the values measured by Rudolph (2010) using Raman spectroscopy, at 296 K. A comparison of these values to the data reported in this thesis is shown in Figure 4.11, which indicates that the literature values of $pK_{aq,D3PO4}$ at 298 K from Paabo and Bates (1970) and McDougall and Long (1962) are approximately 0.08 units lower than the one reported in this study, however the value reported by Rudolph (2010) matches the one reported in this study. Past
Figure 4.8. First acid ionization constants for phosphoric acid in H\textsubscript{2}O and D\textsubscript{2}O, pK\textsubscript{aq} vs. \( T \): (○) H\textsubscript{3}PO\textsubscript{4} and (□) D\textsubscript{3}PO\textsubscript{4}. Solid lines are the fitted density models in Table 4.6, equations (4.24) and (4.26)
Figure 4.9. Comparison values of $\Delta pK_{aq}$ for $\text{H}_3\text{PO}_4$ ($\text{D}_2\text{PO}_4^-$) (●) and $\text{CH}_3\text{COOH}$ ($\text{CH}_3\text{COOD}$) (▲), both from this study to $\text{H}_2\text{PO}_4^-$ ($\text{D}_3\text{PO}_4^-$) (□), as reported by Mesmer and Herting (1978), $\beta$-naphthol (○) and $\text{B(OH)}_3$ ($\text{B(OD)}_3$) (▼), as reported by Bulemela and Tremaine (2009), and $\text{HSO}_4^-$ ($\text{DSO}_4^-$) (△), as reported by Lietzke and Stoughton (1963). The data point for $\text{CH}_3\text{COOH}$ ($\text{CH}_3\text{COOD}$) at 298.15 K was taken from Martin and Butler (1939).
Figure 4.10. Comparison values of $\Delta pK_{aq}$ for $\text{H}_3\text{PO}_4$ ($\text{D}_2\text{PO}_4$) (●) and $\text{CH}_3\text{COOH}$ ($\text{CH}_3\text{COOD}$) (▲), both from this study to $\text{H}_2\text{PO}_4^-$ ($\text{D}_2\text{PO}_4^-$) (□), as reported by Mesmer and Herting (1978), and $\beta$-naphthol (⊙) and $\text{B(OH)}_3$ ($\text{B(OD)}_3$) (▽), as reported by Bulemela and Tremaine (2009) (expanded version). The data point for $\text{CH}_3\text{COOH}$ ($\text{CH}_3\text{COOD}$) at 298.15 K was taken from Martin and Butler (1939).
Figure 4.11. Comparison of experimental values for the first ionization constant of phosphoric acid in $\text{D}_2\text{O}$, $\text{pK}_{\text{aq,D}3\text{PO}_4}$ vs. $T$ (with literature values): (●) This work; (X) Paabo and Bates (1970); (△) McDougall and Long (1962) (▽) Rudolph (2010). The solid line is the fit of the density model, equations (4.24) and (4.26), to this study, Table 4.6.
measurements of $pK_{aq,H_3PO_4}$ using potentiometry have shown deviations from values measured using conductivity (see above). Moreover, the procedure used by Paabo and Bates (1970) estimated the molalities of the dissociated and undissociated forms of $D_3PO_4$ in solution in their calculations, which they have said can introduce “major uncertainty” in the determination of $pK_{aq,D_3PO_4}$. The experimental conductivity procedure reported by McDougall and Long (1962) used values of $\Lambda^o$ for species in $D_2O$, estimated from corresponding values in $H_2O$ (since no measured values in $D_2O$ were known to exist at the time). This most likely affected the accuracy of their value of $pK_{aq,D_3PO_4}$ at 298 K. Based on these reports by Paabo and Bates and McDougall and Long, and the consistency of our value of $pK_{aq,D_3PO_4}$ with that reported by Rudolph (2010), we decided to fix the value of $\Delta a_d$ in equation (4.33), to the experimental data point from this work, $\Delta pK_{aq}(298.174)$:

$$\Delta \log[K_{aq}] - \Delta \log[K_{aq}(298.174)] = \Delta b_d \left( \frac{1}{T} - \frac{1}{298.174} \right) + \Delta c_d \left( \frac{1}{T^2} - \frac{1}{298.174^2} \right) + \Delta e_d \cdot (\log[\rho_{D_2O}] - \log[\rho_{D_2O,298.174}]) \quad (4.26)$$

$\Delta b_d$, $\Delta c_d$ and $\Delta e_d$ were used as adjustable parameters and $\rho_{D_2O}$ is the density of $D_2O$, calculated from the equation of state by Hill (1982). Values of the parameters for $\Delta pK_{aq}$ in equation (4.26), fitted to the experimental data in Table 4.3 are tabulated in Table 4.6. Calculated values of $pK_{aq}$ for $D_2O$ were obtained by adding calculated values of $pK_{aq}$ from equation (4.24) to those calculated values of $\Delta pK_{aq}$ in equation (4.26). These results are plotted in Figure 4.12. The maximum deviation between experimental and predicted values of $pK_{aq,D_3PO_4}$ was no greater than ± 0.06.
Figure 4.12. Deviations between the experimental values and fitted "density" model for the first ionization constant of phosphoric acid in D$_2$O, $[\text{pK}_{\text{aq},\text{D}_3\text{PO}_4}^{\text{expt}} - \text{pK}_{\text{aq},\text{D}_3\text{PO}_4}^{\text{pred}}]$ vs. $T$. 
Figure 4.9 compares values of $\Delta pK_{aq}$ for phosphoric acid to other high temperature and pressure values of $\Delta pK_{aq}$ previously reported by Mesmer and Herting (1978), Lietzke and Stoughton (1963), Bulemela and Tremaine (2009) and the work presented in Chapter 3 for acetic acid. The solid lines in this Figure are the calculated values of $\Delta pK_{aq}$, which were obtained from equations (3.14) (for CH$_3$COOD) and equation (4.26) (for D$_3$PO$_4$). In agreement with the trend observed by Mesmer and Herting and that reported in Chapter 3, the values of $\Delta pK_{aq}$ reported for D$_2$PO$_4^-$ and CH$_3$COOD at 423 K are approximately 0.1 unit lower than those at 298 K, whereas for D$_3$PO$_4$, the value of $\Delta pK_{aq}$ at 298 K is approximately equal to those seen at higher temperatures, $\Delta pK_{aq} = 0.365 \pm 0.004$. Lietzke and Stoughton’s (1963) values of $\Delta pK_{aq}$ are relatively temperature independent from 298 to 373 K, but then decrease sharply with increasing temperature.
CHAPTER 5
DEUTERIUM ISOTOPE EFFECTS ON IONIC HYDRATION

5.1 Limiting Molar Conductivity as a Function of Temperature and Viscosity

Extensive conductivity measurements in H$_2$O at 298 K have clearly shown that ionic mobilities do not follow the relationship shown by Stokes’ law, equation (1.41):

$$\lambda_i^\circ \cdot \eta = \frac{F \cdot e \cdot z}{f_b \cdot \pi \cdot R_i},$$

which states that the limiting ionic conductivity, $\lambda_i^\circ$, of an ion in solution should be inversely related to its ionic radius, $R_i$ (Kay, 1990). Studies by Nakahara and Ibuki (1986), Marshall (1987b), Oelkers and Helgeson (1988) and Zimmerman et al. (2007, 2009) have also shown that the migration of a specific ion in aqueous solution at elevated temperature does not follow equation (5.1) as a function of solvent viscosity. This is due to the “structured” nature of water, which consists of hydrogen-bonded networks that are highly dependent upon temperature and pressure, and the behavior of ions in solution. Ions in solution are hydrated, and cause the solvent molecules to arrange themselves around the ion. The hydration shells have a mean density different than that seen for neat water (Marcus, 2009).

Kay (1990) has identified three main categories of ions in solution: “structure breaking”, “structure making” and “hydrophobic”, whose definition is based on the ion’s ability to influence the hydrogen-bonding network of the hydration sphere surrounding the ion. “Structure breaking” ions have a lower surface charge density, which is not high enough to cause the hydrated water molecules around the ion to become structured. The result is that structure breakers have an ionic mobility that is greater than that predicted
by Stokes’ law, equation (5.1). “Structure makers” have a high surface charge density, which completely orients the hydrated water molecules around the ion. This causes ionic mobilities for structure making ions to be less than those predicted by Stokes’ law. Finally, “hydrophobic” ions have a large co-sphere of solvent molecules, which are highly ordered, resulting in ionic mobilities lower than those predicted by Stokes’ law. In addition, Marcus (2009), has compiled an extensive number of viscosity $B$–coefficients for ions, which can be used to define their “structure making” and “structure breaking” tendencies in aqueous solution.

Using the procedure of Kay, Evans, and their co-workers (Kay and Evans, 1965; Broadwater and Evans, 1974; Broadwater and Kay, 1975; Kay, 1991), we decided to probe the relative differences in ionic hydration of salt solutions between D$_2$O and H$_2$O using the Walden product ratio, equation (1.46):

$$R_{\text{Walden}}^{D/H} = \frac{(\Lambda^\circ \cdot \eta)_{D_2O}}{(\Lambda^\circ \cdot \eta)_{H_2O}} = \frac{R_{\text{stokes,H}_2O}}{R_{\text{stokes,D}_2O}},$$

where $R_{\text{stokes}}$ is the effective Stokes radius of the species in the corresponding solvent. Values of $R_{\text{Walden}}^{D/H} > 1$ correspond to more efficient transport in D$_2$O relative to H$_2$O, than predicted by Stokes’ law. For simple cations and anions, values of $R_{\text{Walden}}^{D/H} > 1$ are thought to arise from two effects: (i) a hydration sphere of an ion in H$_2$O which is larger than that in D$_2$O; or (ii) a greater disruption of hydrogen bonds in liquid D$_2$O by “structure breaking” ions which lowers the local viscosity more (Kay, 1991). This second effect arises because hydrogen bonding in heavy water is stronger than that in light water, at near-ambient conditions (Friedman and Krishnan, 1973). The opposite
arguments for “structure making” ions were used to interpret values of $R_{\text{Walden}}^{\text{D/H}} < 1$ (Kay, 1991).

As the temperature increases, the effects of hydrogen bonding diminish more in D$_2$O than in H$_2$O (Foustoukos and Mysen, 2012). Therefore, for “structure breaking” ions, there will be more long-range polarization effects in D$_2$O vs. H$_2$O, which will increase the effective Stokes’ radius for the ion in D$_2$O vs. H$_2$O. The expected result will be a decreasing value of $R_{\text{Walden}}^{\text{D/H}}$ with increasing temperature. For “structure making” ions, there will be less and less ion-localized solvent structure and a gradual reduction in the effective Stokes’ radius for a species in D$_2$O as temperature increases, when compared to that in H$_2$O. The expected result will therefore be an increasing value of $R_{\text{Walden}}^{\text{D/H}}$ with increasing temperature.

Figures 5.1 to 5.4 show values of the Walden product ratio for the solutions of NaCl, KCl, NaCH$_3$COO, KD$_2$PO$_4$/KH$_2$PO$_4$, DCl/HCl, NaOH/NaOD and KOD/KOH, plotted as a function of temperature. For the salt solutions: NaCl, KCl, NaCH$_3$COO and KD$_2$PO$_4$/KH$_2$PO$_4$, values of $R_{\text{Walden}}^{\text{D/H}}$ are approximately unity at 298 K, consistent with Walden’s rule, to within our combined uncertainty of approximately ± 5%. The Walden product ratios for NaCl and NaCH$_3$COO both reach a shallow maximum at approximately 423 K ($R_{\text{Walden}}^{\text{D/H}} = 1.07$ and 1.08 for NaCl and NaCH$_3$COO, respectively). With increasing temperature, values of $R_{\text{Walden}}^{\text{D/H}}$ for NaCl and NaCH$_3$COO then decrease to values below unity at 548 K ($R_{\text{Walden}}^{\text{D/H}} = 0.87$ and 0.93 for NaCl and NaCH$_3$COO, respectively). Values of $R_{\text{Walden}}^{\text{D/H}}$ for KCl and KD$_2$PO$_4$/KH$_2$PO$_4$, however, reach no noticeable maximum, at least to within our combined uncertainty of approximately ± 5%.
Figure 5.1. Walden product ratios, $(\Lambda^0 \cdot \eta)_{\text{D}_2\text{O}} / (\Lambda^0 \cdot \eta)_{\text{H}_2\text{O}}$ vs. $T$, for (□) NaCl (values reported in Chapter 3); and (■) KCl (values reported in Chapter 4). The solid lines represent lines of best fit.
Figure 5.2. Walden product ratios, \((\Lambda^\circ \cdot \eta)_{D_2O} / (\Lambda^\circ \cdot \eta)_{H_2O}\) vs. \(T\), for (◊) NaCH₃COO (values reported in Chapter 3); and (◇) KD₂PO₄/KH₂PO₄ (values reported in Chapter 4). The solid lines represent lines of best fit.
Figure 5.3. Walden product ratios, \((\Lambda^0 \cdot \eta)_{D2O} / (\Lambda^0 \cdot \eta)_{H2O}\) vs. \(T\), for (Δ) HCl/DCI (values reported in Chapter 3); and (∆) HCl/DCI (values reported in Chapter 4). The solid line represents a line of best fit.
Figure 5.4. Walden product ratios, $(\Lambda^\circ \cdot \eta)_{D2O} / (\Lambda^\circ \cdot \eta)_{H2O}$ vs. $T$, for (●) NaOH/NaOD (values reported in Chapter 3); and (○) KOH/KOD (values reported in Chapter 4). The solid line represents a line of best fit.
Values of $R_{\text{Walden}}^{D/H}$ for DCl/HCl, NaOH/NaOD and KOD/KOH continually increase with increasing temperature, approaching unity at 571 K. The exception is the value of $R_{\text{Walden}}^{D/H}$ for KOD/KOH at 423.295 K. This is likely due to the suspected contamination of the solutions with CO$_2$(g), which was discussed in Chapter 4.

According to the inverse relationship between $R_{\text{Walden}}^{D/H}$ and $R_{\text{stokes}}$, equation (5.2), the increase in values of $R_{\text{Walden}}^{D/H}$ as a function of temperature indicates that the effective Stokes’ radius for NaCl and NaCH$_3$COO in D$_2$O, relative to H$_2$O, gets smaller as the temperature increases from 298 to 423 K. At temperatures greater than 423 K, the reverse trend occurs, where the effective Stokes’ radii for each species in D$_2$O, relative to H$_2$O, becomes larger. The relatively consistent values of $R_{\text{Walden}}^{D/H}$ as a function of temperature for KCl and KD$_2$PO$_4$/KH$_2$PO$_4$ indicate that there is no significant change in the effective Stokes’ radius of each of these species as a function of temperature. For DCl/HCl, NaOH/NaOD and KOD/KOH, the Grothhuss proton hopping mechanism described by Conway et al. (1956) and Tada et al. (1992) contributes to the enhanced mobility of the ions. At lower temperatures, this process is thought to be more effective in H$_2$O than in D$_2$O (Tada et al., 1992).

5.2 Limiting Ionic Molar Conductivity as a Function of Temperature and Viscosity

To investigate deviations from Walden’s rule further, we require values of limiting single-ion molar conductivities, $\lambda^\circ$, from values of $\Lambda^\circ$, using equation (1.40):

$$\lambda^\circ_v = t^\circ_v \cdot \Lambda^\circ$$  
(5.3)
\[
\lambda_+^\circ = t_+^\circ \cdot \Lambda^\circ = (1 - t_-^\circ) \cdot \Lambda^\circ
\]  
(5.4)

where \( t^\circ \) is the transference number of the ion at infinite dilution and \( \lambda^\circ \) is the corresponding limiting ionic molar conductivity of the ion (Robinson and Stokes, 1965).

For solutions not at infinite dilution, equation (5.4) takes the form:

\[
\lambda_+ = t_+ \cdot \Lambda
\]
(5.5)

Values of \( t_+ \) for Na\(^+\) at concentrations of 0.1 mol·kg\(^{-1}\) have been reported, up to 423 K, in H\(_2\)O (Longsworth, 1932; Allgood and Gordon, 1942; Smith and Dismukes, 1964). The values of Smith and Dismukes are the only experimental values of transference numbers for Na\(^+\) above 373 K. Smith and Dismukes (1963, 1964) have shown that values of \( t_+ \) for Na\(^+\) can be represented by a linear correlation of the following form:

\[
\log \left( \frac{1 - t_-}{t_+} \right) = 0.0591 \cdot \left( \frac{1000}{T} \right) + 0.0043
\]
(5.6)

Values reported by Allgood and Gordon (1942) indicate that, up to 318 K, the correlation dependence of \( t_- \) for Cl\(^-\) is represented by: \((t_-^\circ)/(t_-) = (0.9822 \pm 0.0002)\) for 0.1 M Cl\(^-\) in H\(_2\)O.

Following Quist and Marshall (1965) and others, we assumed that equation (5.6) is valid at temperatures up to 673 K, and calculated corresponding values of \( t_- \) for the anion (Cl\(^-\)) using the relation:

\[
t_+ + t_- = 1
\]
(5.7)

Assuming the ratio of \( t^\circ/t \) equals 0.9822 at all temperatures, values of \( t_- \) for Cl\(^-\) calculated from equation (5.7) were used to determine values of \( t_-^\circ \) for Cl\(^-\) as a function of temperature. Using equation (5.4), values of \( \lambda_-^\circ \) for Cl\(^-\) were then calculated, using the experimental values of \( \Lambda^\circ \) for NaCl reported in Chapter 3. The values of \( \lambda_-^\circ \) for Cl\(^-\) were
then subsequently used to calculate values of $\lambda_+^\circ$ for $\text{H}^+$ from the experimental values of $\Lambda^\circ$ for HCl, using equation (1.39):

$$\lambda_+^\circ + \lambda_-^\circ = \Lambda^\circ$$  \hspace{1cm} (5.8)

Corresponding values of $\lambda_-^\circ$ for OH$^-$ and CH$_3$COO$^-$ were also calculated, using the experimental values of $\Lambda^\circ$ for NaOH and NaCH$_3$COO, and the calculated values of $\lambda_+^\circ$ for Na$^+$. Using the resulting values of $\lambda_-^\circ$ for Cl$^-$, values of $\lambda_+^\circ$ for K$^+$ and H$^+$ were calculated from our experimental values of $\Lambda^\circ$ for KCl and HCl reported in Chapter 4. Values of $\lambda_-^\circ$ for OH$^-$ and H$_2$PO$_4^-$ were also calculated, using the experimental values of $\Lambda^\circ$ for KOH and KH$_2$PO$_4$, and the calculated values of $\lambda_+^\circ$ for K$^+$. All these values of $\lambda^\circ$ are tabulated in Tables 5.1 and 5.2 as a function of temperature and H$_2$O viscosity.

To calculate values of $\lambda_+^\circ$ and $\lambda_-^\circ$ for ions in D$_2$O, we have made the assumption that values of $t_+^\circ$ for Na$^+$ in D$_2$O follow the linear correlation of $\log[(1 - t_+)/ t_+]$ vs. $1000/T$ for Na$^+$ in H$_2$O, as reported by Smith and Dismukes (1963, 1964). Using the relationship: $(t_-^\circ)/(t_+) = (0.9822 \pm 0.0002)$ for 0.1 M Cl$^-$ in H$_2$O, values of $t_+^\circ$ for Na$^+$ in H$_2$O were calculated using equation (5.7). These values can be represented by the following linear correlation:

$$\log\left[\frac{1-t_+^\circ}{t_+^\circ}\right] = 0.0576 \cdot \frac{1000}{T} - 0.0105$$ \hspace{1cm} (5.9)

Only two known values of $t_+^\circ$ for Na$^+$ in D$_2$O exist, both at 298.15 K (Longsworth and MacInnes, 1937; Swain and Evans, 1966). Both reported values are the same, within experimental uncertainty, and the more recent value reported by Swain and Evans (1966) was chosen. Using the value of $t_+^\circ$ for Na$^+$ in D$_2$O at 298.15 K, reported by Swain and Evans, in equation (5.9) yields the relationship:
Table 5.1. Calculated values of $\lambda^\circ$ for Cl$^-$, Na$^+$, CH$_3$COO$^-$, H$^+$, and OH$^-$ in H$_2$O as a function of temperature and viscosity using experimental values of $\Lambda^\circ$ for NaCl, NaCH$_3$COO, HCl, and NaOH reported in Table 3.1

<table>
<thead>
<tr>
<th>$T^*$ (K)</th>
<th>$p^*$ (MPa)</th>
<th>$\eta$ (P·s·cm$^{-1}$·mol$^{-1}$)</th>
<th>$\lambda_{\text{Cl}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{Na}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{CH}_3\text{COO}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{H}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{OH}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>0.10</td>
<td>0.0089050</td>
<td>76.385 ± 0.038</td>
<td>50.155 ± 0.054</td>
<td>40.805 ± 0.054</td>
<td>350.115 ± 0.044</td>
<td>199.175 ± 0.062</td>
</tr>
<tr>
<td>368.601</td>
<td>17.5825</td>
<td>0.0030060</td>
<td>200.83 ± 0.51</td>
<td>143.56 ± 0.73</td>
<td>130.59 ± 0.82</td>
<td>645.3 ± 2.7</td>
<td>429.4 ± 5.3</td>
</tr>
<tr>
<td>422.40</td>
<td>17.5023</td>
<td>0.0018770</td>
<td>302.88 ± 0.85</td>
<td>226.7 ± 1.2</td>
<td>211.1 ± 1.4</td>
<td>776.9 ± 3.4</td>
<td>534.5 ± 10.5</td>
</tr>
<tr>
<td>473.35</td>
<td>17.5144</td>
<td>0.0013810</td>
<td>382.9 ± 1.5</td>
<td>296.4 ± 2.1</td>
<td>299.2 ± 2.4</td>
<td>870.9 ± 4.3</td>
<td>666.3 ± 13.4</td>
</tr>
<tr>
<td>498.17</td>
<td>20.8206</td>
<td>0.0012330</td>
<td>426.0 ± 3.4</td>
<td>334.4 ± 4.9</td>
<td>312.8 ± 4.9</td>
<td>889.5 ± 6.9</td>
<td>687.2 ± 14.5</td>
</tr>
<tr>
<td>525.32</td>
<td>17.4945</td>
<td>0.0010880</td>
<td>481.0 ± 2.3</td>
<td>382.8 ± 3.2</td>
<td>358.6 ± 3.3</td>
<td>891.4 ± 4.9</td>
<td>682.7 ± 14.8</td>
</tr>
<tr>
<td>548.44</td>
<td>20.7406</td>
<td>0.0009978</td>
<td>498.3 ± 1.9</td>
<td>400.8 ± 2.7</td>
<td>357.0 ± 4.0</td>
<td>926.4 ± 6.7</td>
<td>730.1 ± 15.7</td>
</tr>
</tbody>
</table>

*Uncertainties in the temperature and pressure are reported in Table 3.1
Table 5.2. Calculated values of $\lambda^\circ$ for Cl$^-$, K$^+$, H$_2$PO$_4^-$, H$^+$, and OH$^-$ in H$_2$O as a function of temperature and viscosity using experimental values of $\Lambda^\circ$ for KCl, KH$_2$PO$_4$, HCl, and KOH reported in Table 4.1

<table>
<thead>
<tr>
<th>$T^\circ$</th>
<th>$p^\circ$</th>
<th>$\eta$</th>
<th>$\lambda_{\text{Cl}^-}^\circ$</th>
<th>$\lambda_{\text{K}^+}^\circ$</th>
<th>$\lambda_{\text{H}_2\text{PO}_4^-}^\circ$</th>
<th>$\lambda_{\text{H}^+}^\circ$</th>
<th>$\lambda_{\text{OH}^-}^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>MPa</td>
<td>P</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
</tr>
<tr>
<td>298.174</td>
<td>20.3024</td>
<td>0.0088590</td>
<td>76.78 ± 0.53</td>
<td>73.45 ± 0.76</td>
<td>31.67 ± 0.77</td>
<td>348.0 ± 1.2</td>
<td>197.7 ± 1.8</td>
</tr>
<tr>
<td>374.216</td>
<td>21.2841</td>
<td>0.0028430</td>
<td>212.34 ± 0.38</td>
<td>189.59 ± 0.54</td>
<td>109.30 ± 0.64</td>
<td>653.1 ± 2.9</td>
<td>442.9 ± 3.8</td>
</tr>
<tr>
<td>423.295</td>
<td>21.3050</td>
<td>0.0018750</td>
<td>303.21 ± 0.54</td>
<td>282.20 ± 0.77</td>
<td>166.55 ± 0.93</td>
<td>780.3 ± 3.7</td>
<td>514.8 ± 4.8</td>
</tr>
<tr>
<td>471.88</td>
<td>21.2994</td>
<td>0.0014000</td>
<td>377.69 ± 0.47</td>
<td>372.53 ± 0.67</td>
<td>195.25 ± 0.74</td>
<td>824.3 ± 3.1</td>
<td>632.5 ± 5.5</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
<td>0.0012340</td>
<td>425.67 ± 0.75</td>
<td>428.0 ± 1.1</td>
<td>230.5 ± 1.2</td>
<td>849.7 ± 4.5</td>
<td>705.2 ± 6.6</td>
</tr>
<tr>
<td>523.56</td>
<td>21.1355</td>
<td>0.0011050</td>
<td>473.6 ± 1.0</td>
<td>451.4 ± 1.4</td>
<td>271.8 ± 1.5</td>
<td>865.3 ± 4.4</td>
<td>758.5 ± 7.1</td>
</tr>
<tr>
<td>548.63</td>
<td>20.1351</td>
<td>0.0009954</td>
<td>499.49 ± 0.85</td>
<td>497.9 ± 1.2</td>
<td>280.5 ± 1.3</td>
<td>868.8 ± 3.8</td>
<td>749.3 ± 7.2</td>
</tr>
<tr>
<td>571.91</td>
<td>21.1465</td>
<td>0.0009089</td>
<td>539.50 ± 1.5</td>
<td>513.3 ± 2.1</td>
<td>340.6 ± 2.3</td>
<td>892.9 ± 4.3</td>
<td>817.6 ± 7.7</td>
</tr>
</tbody>
</table>

*Uncertainties in the temperature and pressure are reported in Table 4.1
\[
\log \left[ 1 - \frac{t_{-}}{t_{+}} \right] = 0.0576 \cdot \left( \frac{1000}{T} \right) - 0.0143,
\]

(5.10)

which was used to calculate values of \( t_{+}^{o} \) for Na\(^+\) in D\(_2\)O as a function of temperature from which values of \( t_{-}^{o} \) for Cl\(^-\) in D\(_2\)O were calculated. Values of \( \lambda_{+}^{o} \) for Cl\(^-\) in D\(_2\)O were then calculated, using the experimental values of \( \Lambda^{o} \) for NaCl in D\(_2\)O, reported in Chapter 3. These were used to calculate values of \( \lambda_{-}^{o} \) for D\(^+\) from the experimental values of \( \Lambda^{o} \) for DC\(_2\). Corresponding values of \( \lambda_{-}^{o} \) for OD\(^-\) and CH\(_3\)COO\(^-\) were also calculated, using the experimental values of \( \Lambda^{o} \) of NaOD and NaCH\(_3\)COO and the calculated values of \( \lambda_{+}^{o} \) for Na\(^+\).

The experimental temperature conditions reported in Chapter 4 do not exactly match those reported in Chapter 3. To derive values of \( \lambda_{+}^{o} \) for K\(^+\) and D\(^+\) and values of \( \lambda_{-}^{o} \) for D\(_2\)PO\(_4\)\(^-\) and OD\(^-\) from the experimental values of \( \Lambda^{o} \) reported in Chapter 4 at the correct temperatures, the calculated values of \( \lambda_{-}^{o} \) for Cl\(^-\) in D\(_2\)O described above were corrected for slight differences in solvent viscosity using Walden’s rule. We have found this to be accurate, to within the experimental uncertainty in the values of \( \lambda_{-}^{o} \) for Cl\(^-\) over this slight change in solvent viscosity. No values of \( \Lambda^{o} \) for NaCl in D\(_2\)O were measured during the acetic acid study at 571 K. Therefore, a correlation between \( \log[\Lambda_{NaCl}^{o}] \) vs. \( \log[\eta_{D2O}] \) was found from our experimental data:

\[
\log[\Lambda_{NaCl}^{o}] = -0.2899 \cdot (\log[\eta_{D2O}])^2 - 2.2502 \cdot \log[\eta_{D2O}] - 1.2779
\]

(5.11)

Equation (5.11) was used to estimate a value of \( \Lambda^{o} \) for NaCl in D\(_2\)O at 571 K. A value of \( \lambda_{-}^{o} \) for Cl\(^-\) in D\(_2\)O was then calculated at this temperature using equation (5.4). All values
of $\lambda_+^o$ and $\lambda_-^o$ for all the ions measured in this project in D$_2$O are reported in Tables 5.3 and 5.4 as a function of temperature and D$_2$O solvent viscosity.

Values of $\lambda_+^o$ and $\lambda_-^o$, for all the species in both H$_2$O and D$_2$O, increase with increasing temperature, which is consistent with the Stokes-Einstein equation (Cappelezze et al., 2007). Values of $\lambda_+^o$ and $\lambda_-^o$ for the ions in H$_2$O are greater than those in D$_2$O, at each experimental temperature. Equation (5.2) has been used to calculate the Walden product ratio, $R_{\text{Walden}}^{\text{D/H}}$, for these ions in D$_2$O and H$_2$O as a function of temperature. The results are plotted in Figures 5.5 to 5.9. These plots show that for several ions (Cl$^-$, Na$^+$, CH$_3$COO$^-$ and D$_2$PO$_4^-$/H$_2$PO$_4^-$), $R_{\text{Walden}}^{\text{D/H}}$ changes as a function of temperature: first increasing, then decreasing. For all these ions, $R_{\text{Walden}}^{\text{D/H}}$ is near unity at 298 K, but increases with an increase in temperature. $R_{\text{Walden}}^{\text{D/H}}$ reaches a maximum values of 1.08 for Cl$^-$ at ~ 370 K, 1.06 for Na$^+$ at ~ 370 K, 1.19 at ~ 495 K for CH$_3$COO$^-$ and 1.15 at ~ 370 K for D$_2$PO$_4^-$/H$_2$PO$_4^-$). As the temperature continues to increase, $R_{\text{Walden}}^{\text{D/H}}$ for all these ions decreases (to values of 0.81 at ~ 570 K for Cl$^-$, 0.88 at ~ 548 K for Na$^+$, 0.99 at ~ 548 K for CH$_3$COO$^-$ and 0.76 at ~ 570 K for D$_2$PO$_4^-$/H$_2$PO$_4^-$). Figures 5.5 to 5.9 also show that for other ions (K$^+$, D$^+$/H$^+$ and OD$^-$/OH$^-$), $R_{\text{Walden}}^{\text{D/H}}$ continues to increase with increasing temperature. At 298 K, values of $R_{\text{Walden}}^{\text{D/H}}$ for K$^+$, D$^+$/H$^+$ and OD$^-$/OH$^-$ all exist close to or below unity (1.00 for K$^+$, 0.87 for D$^+$/H$^+$ and 0.71 for OD$^-$/OH$^-$). As the temperature increases, values of $R_{\text{Walden}}^{\text{D/H}}$ for these species increase. At 571 K, values of $R_{\text{Walden}}^{\text{D/H}}$ are 1.21 for K$^+$, 1.00 for D$^+$/H$^+$ and 0.76 for OD$^-$/OH$^-$. There are inconsistencies in the values of $R_{\text{Walden}}^{\text{D/H}}$ for OD$^-$/OH$^-$, depending on whether values of $\lambda^o$ for OD$^-$/OH$^-$ were calculated.
Table 5.3. Calculated values of $\lambda^\circ$ for Cl, Na$,^\circ$, CH$_3$COO$,^\circ$, D$,^\circ$, and OD$^-$ in D$_2$O as a function of temperature and viscosity using experimental values of $\Lambda^\circ$ for NaCl, NaCH$_3$COO, DCI, and NaOD reported in Table 3.2

<table>
<thead>
<tr>
<th>$T^\circ$ (K)</th>
<th>$P^\circ$ (MPa)</th>
<th>$\eta$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{Cl}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{Na}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{CH}_3\text{COO}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{D}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{OD}}^\circ$ (S·cm$^2$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>0.10</td>
<td>0.0109510</td>
<td>62.830 ± 0.010</td>
<td>41.620 ± 0.014</td>
<td>33.68 ± 0.23</td>
<td>249.27 ± 0.31</td>
<td>117.32 ± 0.16</td>
</tr>
<tr>
<td>368.601</td>
<td>17.5825</td>
<td>0.0035202</td>
<td>182.11 ± 0.61</td>
<td>131.34 ± 0.86</td>
<td>113.87 ± 0.91</td>
<td>461.8 ± 2.5</td>
<td>234.3 ± 3.6</td>
</tr>
<tr>
<td>422.40</td>
<td>17.5023</td>
<td>0.0021679</td>
<td>270.36 ± 0.96</td>
<td>204.1 ± 1.4</td>
<td>204.6 ± 1.5</td>
<td>567.5 ± 3.5</td>
<td>314.0 ± 5.2</td>
</tr>
<tr>
<td>473.35</td>
<td>17.5144</td>
<td>0.0015663</td>
<td>308.5 ± 1.1</td>
<td>240.9 ± 1.5</td>
<td>300.1 ± 1.7</td>
<td>710.6 ± 3.8</td>
<td>553.6 ± 6.9</td>
</tr>
<tr>
<td>498.17</td>
<td>20.8206</td>
<td>0.0013853</td>
<td>322.2 ± 3.4</td>
<td>255.2 ± 4.8</td>
<td>328.6 ± 4.8</td>
<td>709.4 ± 13.3</td>
<td>542.6 ± 8.6</td>
</tr>
<tr>
<td>525.32</td>
<td>17.4945</td>
<td>0.0012100</td>
<td>380.4 ± 1.5</td>
<td>305.5 ± 2.1</td>
<td>332.9 ± 2.3</td>
<td>734.7 ± 4.7</td>
<td>581.4 ± 8.1</td>
</tr>
<tr>
<td>548.44</td>
<td>20.7406</td>
<td>0.0011023</td>
<td>390.1 ± 3.9</td>
<td>316.6 ± 5.5</td>
<td>323.5 ± 5.8</td>
<td>835.0 ± 6.4</td>
<td>651.0 ± 10.2</td>
</tr>
</tbody>
</table>

*Uncertainties in the temperature and pressure are reported in Table 3.2
Table 5.4. Calculated values of $\lambda^o$ for Cl$^-$, K$^+$, D$_2$PO$_4^-$, D$_2^+$, and OD$^-$ in D$_2$O as a function of temperature and viscosity using experimental values of $\Lambda^o$ for KCl, KD$_2$PO$_4$, DCI, and KOD reported in Table 4.2

<table>
<thead>
<tr>
<th>$T^*$ (K)</th>
<th>$p^*$ (MPa)</th>
<th>$\eta$ (P)</th>
<th>$\lambda_{\text{Cl}^-}^o$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{K}^+}^o$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{D}_2\text{PO}_4^-}^o$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{D}_2^+}^o$ (S·cm$^2$·mol$^{-1}$)</th>
<th>$\lambda_{\text{OD}^-}^o$ (S·cm$^2$·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.174</td>
<td>20.3024</td>
<td>0.0108800</td>
<td>63.24 ± 0.45</td>
<td>60.05 ± 0.63</td>
<td>28.30 ± 0.63</td>
<td>245.6 ± 1.3</td>
<td>113.7 ± 1.1</td>
</tr>
<tr>
<td>374.216</td>
<td>21.2841</td>
<td>0.0033263</td>
<td>192.73 ± 0.35</td>
<td>151.89 ± 0.49</td>
<td>108.20 ± 0.61</td>
<td>454.3 ± 2.3</td>
<td>245.8 ± 1.7</td>
</tr>
<tr>
<td>423.295</td>
<td>21.3050</td>
<td>0.0021656</td>
<td>270.65 ± 0.54</td>
<td>261.94 ± 0.77</td>
<td>162.43 ± 0.98</td>
<td>558.7 ± 2.6</td>
<td>210.1 ± 2.1</td>
</tr>
<tr>
<td>471.88</td>
<td>21.2994</td>
<td>0.0015901</td>
<td>303.88 ± 0.60</td>
<td>355.10 ± 0.84</td>
<td>159.47 ± 0.99</td>
<td>669.3 ± 2.9</td>
<td>424.9 ± 3.0</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
<td>0.0013871</td>
<td>321.80 ± 0.66</td>
<td>423.87 ± 0.93</td>
<td>169.72 ± 1.0</td>
<td>733.9 ± 6.4</td>
<td>505.6 ± 3.8</td>
</tr>
<tr>
<td>523.56</td>
<td>21.1355</td>
<td>0.0012307</td>
<td>374.02 ± 0.79</td>
<td>445.2 ± 1.1</td>
<td>223.10 ± 1.2</td>
<td>739.4 ± 4.4</td>
<td>558.2 ± 4.0</td>
</tr>
<tr>
<td>548.63</td>
<td>20.1351</td>
<td>0.0010994</td>
<td>391.13 ± 0.67</td>
<td>503.79 ± 0.94</td>
<td>226.55 ± 1.1</td>
<td>749.8 ± 3.9</td>
<td>550.0 ± 4.1</td>
</tr>
<tr>
<td>571.91</td>
<td>21.1465</td>
<td>0.0009968</td>
<td>400.0 ± 1.3</td>
<td>567.2 ± 1.9</td>
<td>236.4 ± 2.2</td>
<td>787.1 ± 4.5</td>
<td>568.0 ± 4.6</td>
</tr>
</tbody>
</table>

*Uncertainties in the temperature and pressure are reported in Table 4.2
Figure 5.5. Walden product ratios, $(\lambda^o \cdot \eta)_{D_2O} / (\lambda^o \cdot \eta)_{H_2O}$ vs. $T$, for (□) Cl$^-$ (calculated from values reported in Chapter 3); and (■) Cl$^-$ (calculated from values reported in Chapter 4). The solid line represents a line of best fit.
Figure 5.6. Walden product ratios, $(\lambda^\circ \cdot \eta)_{D2O} / (\lambda^\circ \cdot \eta)_{H2O}$ vs. $T$, for (□) Na$^+$ (calculated from values reported in Chapter 3); and (■) K$^+$ (calculated from values reported in Chapter 4). The solid line represents a line of best fit.
Figure 5.7. Walden product ratios, \((\lambda^\circ \cdot \eta)_{\text{D}_2\text{O}} / (\lambda^\circ \cdot \eta)_{\text{H}_2\text{O}}\) vs. \(T\), for (○) \(\text{CH}_3\text{COO}^-\) (calculated from values reported in Chapter 3); and (□) \(\text{D}_2\text{PO}_4^- / \text{H}_2\text{PO}_4^-\) (calculated from values reported in Chapter 4). The solid line represents a line of best fit.
Figure 5.8. Walden product ratios, $(\lambda^0 \cdot \eta)_{\text{D}_2\text{O}} / (\lambda^0 \cdot \eta)_{\text{H}_2\text{O}}$ vs. $T$, for (△) $\text{D}^+ / \text{H}^+$ (calculated from values reported in Chapter 3); and (▲) $\text{D}^+ / \text{H}^+$ (calculated from values reported in Chapter 4). The solid line represents a line of best fit.
Figure 5.9. Walden product ratios, $(\lambda^0 \cdot \eta)_{D2O} / (\lambda^0 \cdot \eta)_{H2O}$ vs. $T$, for (•) OD/\text{OH}^- (calculated from values reported in Chapter 3); and (◇) OD/\text{OH}^- (calculated from values reported in Chapter 4). The solid line represents a line of best fit.
using values of $\Lambda^\circ$ from NaOH or KOH. Reasons for this will be discussed in more detail below.

From equation (5.2), it can be seen that values of $R_{\text{Walden}}^{D/H}$ greater than unity correspond to the effective Stokes’ radius of an ion in H$_2$O greater than the corresponding effective Stokes’ radius of the ion in D$_2$O. For Cl$^-$ (Figure 5.5), Na$^+$ (Figure 5.6), CH$_3$COO$^-$ (Figure 5.7) and D$_2$PO$_4^-$/H$_2$PO$_4^-$ (Figure 5.7), values of $R_{\text{Walden}}^{D/H}$ greater than unity are in the lower temperature range of our studies (from 298 to approximately 370 K for Cl$^-$, Na$^+$ and D$_2$PO$_4^-$/H$_2$PO$_4^-$ and from 298 K to approximately 495 K for CH$_3$COO$^-$), which supports Kay, Evans, and co-workers (Kay and Evans, 1965; Swain and Evans, 1966; Broadwater and Evans, 1974; Broadwater and Kay, 1975; Kay, 1991) description of ions that are “structure breaking”, where the presence of the ion causes greater breakdown of ion-localized hydrogen bonding in D$_2$O vs. H$_2$O. Furthermore, values of $R_{\text{Walden}}^{D/H}$ as a function of temperature for each of Cl$^-$, Na$^+$, CH$_3$COO$^-$ and D$_2$PO$_4^-$/H$_2$PO$_4^-$ show that, at temperatures above ~ 450 K, the decreasing strength of hydrogen bonding in D$_2$O vs. H$_2$O enhances long-range polarization effects, causing $R_{\text{stokes,D2O}}$ to be greater than $R_{\text{stokes,H2O}}$.

$R_{\text{Walden}}^{D/H}$ for K$^+$ (Figure 5.6) has been found to be less than unity at 298 K. Kay, Evans, and co-workers (Kay and Evans, 1965; Swain and Evans, 1966; Broadwater and Evans, 1974; Broadwater and Kay, 1975; Kay, 1991) description of “structure making” supports this result, where there the presence of the ion causes an increase of ion-localized hydrogen bonding in D$_2$O vs. H$_2$O. The continued increase of $R_{\text{Walden}}^{D/H}$ as a
function of temperature for K$^+$ indicates that there is a decreasing strength of hydrogen bonding in D$_2$O vs. H$_2$O, causing $R_{\text{stokes,H}_2\text{O}}$ to be greater than $R_{\text{stokes,D}_2\text{O}}$.

Recent measurements by Jeffrey Plumridge (2013) under similar conditions have shown discrepancies in values of $\Lambda^\circ$ for NaCl in D$_2$O by up to 30%. Reasons for this difference are unknown at this time but are under investigation. The values of $\Lambda^\circ$ for NaCl in D$_2$O are used to calculate values of $\lambda^+\circ$ for Na$^+$, used to determine values of $\lambda^\circ$ for all the other ions in D$_2$O using limiting transport numbers (see equations (5.3) to (5.8)). This could account for the differences in our Walden product ratios for OD$^-$ above 450 K, Figure 5.9

5.3 Hydrogen Bonding and Proton Hopping Mechanisms

The continued increase of $R_{\text{Walden}}^{\text{D/H}}$ as a function of increasing temperature for D$^+/H^+$, which we have shown in Figure 5.8, can be described in terms of the Grotthuss (“proton-hopping”) mechanism. The Grotthuss mechanism is known to include the diffusion of protons along the hydrogen bond network in bulk water by the rearrangement of hydrogen bonds within the solvent (Conway et al., 1956; Agmon, 1995; Day et al., 2000; Swanson et al., 2007). This mechanism, shown in Figure 1.9, postulates that the transfer of a proton from H$_3$O$^+$ to H$_2$O must be preceded by a rotation of the hydronium ion. In the case of where D$_2$O is the solvent, there is a higher activation energy for the pre-rotation step, when compared with H$_2$O (Tada et al., 1992, 1993). This higher activation energy would result in values of $R_{\text{Walden}}^{\text{D/H}}$ less than unity at lower temperatures. As the average number of intermolecular hydrogen bonds in D$_2$O versus H$_2$O decreases with increasing temperature, a more effective proton-hopping mechanism for D$^+$ makes it
more similar to H⁺. Therefore, values of $R^{D/H}_{Walden}$ would be expected to increase towards values of unity.

For OD⁻/OH⁻, values of $R^{D/H}_{Walden}$ also increase as a function of temperature, as shown in Figure 5.9. The results of Tada et al. (1993) have concluded that the transfer of a proton from H₂O to OH⁻ includes an activation energy in the pre-rotation step, which is higher than that seen in the transfer of a proton from H₃O⁺ to H₂O. Svishchev and Plugatyr (2005) have done extensive molecular dynamic calculations on the hydroxyl radical in water as a function of temperature, and have determined that the radical behaves as a distinct species, occupying “holes” in the tetrahedral arrangement of the solvent molecules at low temperatures, but behaves indistinguishably from H₂O as the critical point is approached. Our results support this, where values of $\lambda^o$ for OH⁻ are lower than the corresponding values of $\lambda^o$ for H⁺ at each set of temperatures and pressures, and similar results are seen when values of $\lambda^o$ for OD⁻ are compared with those of D⁺. By comparing the mechanism of transfer of a deuteron from D₂O to OD⁻ to the transfer of a proton from H₂O to OH⁻, Tada et al. (1993) observed that the activation energy for the heavy water from 283 to 313 K is larger than that in light water, due to the stronger hydrogen bonding in D₂O. Values of $R^{D/H}_{Walden}$ for OD⁻/OH⁻ reported here start below unity at 298 K and increase with increasing temperature, indicating a more efficient proton-hopping for the deuterated species as the hydrogen bond strength in D₂O, with respect to H₂O, weakens.

It was mentioned above that there are inconsistencies observed in values of $R^{D/H}_{Walden}$ for OD⁻/OH⁻ as a function of temperature, depending on whether the values of $R^{D/H}_{Walden}$ for
OD'/OH' were calculated from values of Λ° for NaOH/NaOD or KOH/KOD, using equation (5.8). These inconsistencies are most likely due to experimental uncertainties in the measurement of the conductivities of NaOH/NaOD or KOH/KOD. Nevertheless, these measurements of values of Λ°, and then corresponding values of λ° for ions in D₂O, are the first to be reported at temperatures above 373 K. These quantitative data yield insights about the effects of ion solvation in D₂O versus H₂O at elevated temperatures.
6.1 Modelling $\Delta pK_{aq}$ as a Function of Temperature

6.1.1 The Born-Haber Cycle

A useful way to represent $\Delta pK_{aq}$ is through a Born-Haber solvation cycle, which is presented in Figure 6.1. In a Born-Haber solvation cycle, the ionization reaction within the solvent is considered to arise from the gas-phase ionization, and the solvation of each individual species. The deuterium isotope effect for an acid, "HA", is given by the sum of the steps, i.e.,

$$\log \left( \frac{K_{a,H_2O}}{K_{a,D_2O}} \right) = -\ln 10 \frac{R \cdot T}{[\Delta \Delta G_r^\circ(DA,g) + \Delta \Delta \text{solv} G^\circ(D^+,aq)}$$

$$+\Delta \Delta \text{solv} G^\circ(A^-,aq) - \Delta \Delta \text{solv} G^\circ(DA,aq)] , \quad (6.1)$$

where $\Delta \Delta G_r^\circ(DA,g) = [\Delta G_r^\circ(DA,g) - \Delta G_r^\circ(HA,g)]$, and the $\Delta \Delta \text{solv} G^\circ$ terms have their corresponding definitions. The gas-phase ionization step, $\Delta \Delta G_r^\circ(DA,g)$, in equation (6.1) can be represented by differences in the reduced masses of O-D versus O-H, which are temperature insensitive. The $\Delta \Delta \text{solv} G^\circ$ terms in equation (6.1) depend highly upon temperature since short-range hydration and long-range polarization effects within the solvent are highly temperature dependent.
Figure 6.1  A Born-Haber solvation cycle for the ionization of an acid in H$_2$O and D$_2$O. a) Figure not including the presence of the solvent; b) Figure including the presence of the solvent.
Steps in the Born-Haber cycle: $\Delta\Delta G^\circ_r(DA,g)$, $\Delta\Delta_{solv} G^\circ(D^+,aq)$, $\Delta\Delta_{solv} G^\circ(A^-,aq)$ and $-\Delta\Delta_{solv} G^\circ(DA,aq)$, can be modelled using semi-empirical equations. Our attempt to model values of $\Delta pK_{aq}$ as a function of temperature is based on the simple descriptions of zero-point energy effects described in the following sections.

### 6.1.2 Modelling and Approximation Techniques

The modelling of deuterium isotope effects began with Bigeleisen and Mayer (1947), who developed a quantum mechanical description of the differences in free energy of formation of gaseous isotopic molecules, which were later used to calculate isotopic differences in activation energies and thermodynamic properties. These were eventually used to relate differences in Gibbs free energies of reaction to differences in the reduced masses, and therefore zero-point energies, of a harmonic oscillator in the gas phase (Bigeleisen, 1949, 1953, 1955). Melander (1960) then developed a simple harmonic-oscillator approximation for estimating values of $\Delta pK_a$ as a function of temperature in the gas phase. This treatment assumed that only the ground state vibrational levels are occupied, and that only the chemical bonds in product and reactant species, which are directly involved in the ionization reaction, contribute to the difference in ionization constants. The result is expressed as:

$$\log\left[\frac{K_{a,H_2O}}{K_{a,D_2O}}\right] = -\frac{h \cdot c}{\ln 10 \cdot 2 \cdot k_B \cdot T} \left(\sum_i \Delta \nu_{O-H} - \sum_i \Delta \nu_{O-D}\right), \quad (6.2)$$

where $h$ is Planck's constant, $c$ is the velocity of light, $k_B$ is Boltzmann's constant and $\Delta \nu$ is the change in vibrational frequency of a given normal mode between products and reactants of protonated and deuterated species in solution, which corresponds to each
O-H or O-D bond. By applying the linear harmonic oscillator approximation to the O-H stretching frequency, and ignoring all others, one obtains:

\[
\log \left( \frac{K_{a,\text{H}_2\text{O}}}{K_{a,\text{D}_2\text{O}}} \right) = -\frac{h \cdot c_v}{\ln 10 \cdot 2 \cdot k_B \cdot T} \cdot \Delta \nu_{\text{O-H}} \cdot \left[ 1 - \left( \frac{\mu_{\text{OH}}}{\mu_{\text{OD}}} \right)^{1/2} \right]
\]

\[
= -\frac{h \cdot c_v}{\ln 10 \cdot 2 \cdot k_B \cdot T} \cdot (0.276 \cdot \Delta \nu_{\text{O-H}}),
\]

(6.3)

where, \( \mu \) represents reduced mass of either O-H or O-D.

Mesmer and Herting (1978) have used equation (6.3) to estimate values of \( \Delta pK_a \) for the ionization of \( \text{D}_2\text{O(l)} \) and \( \text{D}_2\text{PO}_4^-(aq) \) as a simple function of temperature:

\[\text{D-OD} \rightleftharpoons \text{D}^+ + \text{OD}^- \] (6.4)

\[(\text{DO-PO}_2^-)-\text{OD} \rightleftharpoons \text{D}^+ + (\text{DO-PO}_2^-)-\text{O}^- \] (6.5)

By applying the crude assumption that only the O-D or O-H bond is broken, and that solvation effects can be ignored. Experimental values of \( \Delta pK_a \) for \( \text{D}_2\text{PO}_4^- \), reported by Mesmer and Herting, are 0.54 and 0.42 at 298 and 573 K, respectively. Their estimated value of \( \Delta pK_a \) at 298 K (\( \Delta pK_a = 0.74 \)), calculated using a cited stretching frequency of 2600 cm\(^{-1}\), does not correlate well with their experimental value at 298 K. However, at 573 K, their estimated value (\( \Delta pK_a = 0.39 \)) is much closer to their experimental one.

### 6.1.3 Modelling of Deuterium Isotope Effects of \text{CH}_3\text{COOD} and \text{D}_3\text{PO}_4

Initially, our modeling of deuterium isotope effects for \( \text{D}_3\text{PO}_4 \) began by repeating the initial estimations reported by Mesmer and Herting (1978), using equation (6.3). To keep the results consistent for \( \text{D}_3\text{PO}_4 \), we used a reported O-H stretching frequency of
approximately 2600 cm$^{-1}$ for H$_3$PO$_4$ in H$_2$O, cited by Mesmer and Herting, to estimate values of $\Delta pK_{aq}$ for D$_3$PO$_4$ as a function of temperature.

We also used equation (6.3) to estimate values of $\Delta pK_{aq}$ for CH$_3$COOD as a function of temperature. A recent paper by Johnson et al. (2005) has shown that the peak corresponding to the O-H stretching frequency in H$_2$O is broad, centered around $\nu = 3000$ cm$^{-1}$, which corresponds to symmetric and asymmetric stretching in H$_2$O. Also, according to Semmler and Irish (1988), the majority of studies after 1940 on the vibrational spectra of aqueous acetic acid focused on the low-wavenumber region of the spectra ($\nu < 1800$ cm$^{-1}$). Therefore, a more absolute value for the O-H stretching frequency of an acetic acid monomer ($\nu = 3523$ cm$^{-1}$) in H$_2$O had to be taken from an older literature source (Davies and Sutherland, 1938), to use in equation (6.3) to calculate predicted values of $\Delta pK_a$ for CH$_3$COOD as a function of temperature.

Comparisons of the experimental and predicted values of $\Delta pK_{aq}$ for CH$_3$COOD and D$_3$PO$_4$ as a function of temperature are shown in Tables 6.1 and 6.2. A comparison of experimental and predicted values of $\Delta pK_{aq}$ show that equation (6.3) gives only a crude approximation at lower temperatures. This approximation, however, seems to improve with increasing temperature.

Bunton and Shiner (1961) have suggested that deuterium isotope effects on acid ionization arise primarily from changes in the zero point energy difference, which are affected by changes in hydrogen bond strength. They have shown that values of $\Delta pK_a$ for several weak acids at 298 K can be estimated by considering all the vibrational frequencies of O-H bonds in an aqueous solution, associated with the product and reactant species (equation (1.98)):
Table 6.1. Comparison of experimental values of $\Delta pK_{aq}$ ($\Delta pK_{aq,\text{exp}}$) for acetic acid as a function of temperature, with predicted values of $\Delta pK_{aq}$ ($\Delta pK_{aq,\text{pred}}$) calculated using equation (6.3), as reported by Mesmer and Herting (1978), and calculated using equations (6.6) to (6.8), the method reported by Bunton and Shiner (1961)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$\Delta pK_{aq,\text{exp}}$</th>
<th>$\Delta pK_{aq,\text{pred}}^*$</th>
<th>$\Delta pK_{aq,\text{pred}}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.85</td>
<td>0.52</td>
<td>1.02</td>
<td>0.50</td>
</tr>
<tr>
<td>368.58</td>
<td>0.43</td>
<td>0.83</td>
<td>0.40</td>
</tr>
<tr>
<td>422.40</td>
<td>0.44</td>
<td>0.72</td>
<td>0.35</td>
</tr>
<tr>
<td>473.35</td>
<td>0.45</td>
<td>0.64</td>
<td>0.32</td>
</tr>
<tr>
<td>498.17</td>
<td>0.49</td>
<td>0.61</td>
<td>0.30</td>
</tr>
<tr>
<td>525.32</td>
<td>0.45</td>
<td>0.58</td>
<td>0.28</td>
</tr>
<tr>
<td>548.44</td>
<td>0.50</td>
<td>0.55</td>
<td>0.27</td>
</tr>
</tbody>
</table>

*Values predicted using equation (6.3), as reported by Mesmer and Herting (1978)

**Values predicted using equations (6.6) to (6.8), the method reported by Bunton and Shiner (1961)
Table 6.2. Comparison of experimental values of $\Delta pK_{aq}$ ($\Delta pK_{aq,exp}$) for phosphoric acid as a function of temperature, with predicted values of $\Delta pK_{aq}$ ($\Delta pK_{aq,pred}$) calculated using equation (6.3), as reported by Mesmer and Herting (1978), and calculated using equations (6.6), (6.9) and (6.10), the method reported by Bunton and Shiner (1961)

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\Delta pK_{aq,exp}$</th>
<th>$\Delta pK_{aq,pred}^*$</th>
<th>$\Delta pK_{aq,pred}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.17</td>
<td>0.37</td>
<td>0.75</td>
<td>0.37</td>
</tr>
<tr>
<td>374.22</td>
<td>0.34</td>
<td>0.60</td>
<td>0.30</td>
</tr>
<tr>
<td>423.30</td>
<td>0.33</td>
<td>0.53</td>
<td>0.26</td>
</tr>
<tr>
<td>471.88</td>
<td>0.34</td>
<td>0.48</td>
<td>0.23</td>
</tr>
<tr>
<td>498.02</td>
<td>0.36</td>
<td>0.45</td>
<td>0.22</td>
</tr>
<tr>
<td>523.56</td>
<td>0.36</td>
<td>0.43</td>
<td>0.21</td>
</tr>
<tr>
<td>548.63</td>
<td>0.34</td>
<td>0.41</td>
<td>0.20</td>
</tr>
<tr>
<td>571.91</td>
<td>0.31</td>
<td>0.39</td>
<td>0.19</td>
</tr>
</tbody>
</table>

*Values predicted using equation (6.3), as reported by Mesmer and Herting (1978)

**Values predicted using equations (6.6), (6.9) and (6.10), the method reported by Bunton and Shiner (1961)
\[ \Delta pK_a = -\log \left[ \frac{K_{a,\text{H}_2\text{O}}}{K_{a,\text{D}_2\text{O}}} \right] = \sum \nu_{\text{O-H},\text{reactants}} - \sum \nu_{\text{O-H},\text{products}} \cdot \frac{12.53 \cdot T}{\nu}, \]  

(6.6)

where the following rules are followed: (i) each water molecule will donate and accept two hydrogen bonds, (ii) solute molecules will only hydrogen bond with solvent molecules, (iii) a solute more basic than water will accept hydrogens from the solvent, (iv) solute molecules more acidic than water will donate hydrogens to the solvent and (v) there must be symmetry between the number of hydrogen bonds donate and accepted on each side of the chemical equation (Bunton and Shiner, 1961).

As shown in Figure 1.20, using the ionization of acetic acid as an example, H\textsubscript{2}O has a co-ordination number of four at 298 K, whose stretching frequencies are represented by \( \nu_{\text{H},3} \). H\textsubscript{3}O\textsuperscript{+} has a co-ordination number of three, whose stretching frequencies are represented by \( \nu_{\text{H},5} \). Acetic acid has two hydrogen-bonded water molecules, which are represented by stretching frequencies \( \nu_{\text{H},1} \) and \( \nu_{\text{H},2} \), where \( \nu_{\text{H},1} \) corresponds to the H-O stretching frequency between the acidic proton and a neighboring H\textsubscript{2}O molecule and \( \nu_{\text{H},2} \) corresponds to the O-H stretching frequency between the hydroxyl oxygen atom on the acid and a neighboring H\textsubscript{2}O molecule. Finally, the acetate anion has four hydrogen-bonded water molecules, represented by the stretching frequency, \( \nu_{\text{H},4} \). Based on Figure 1.20, \( \nu_{\text{O-H},\text{reactants}} \) and \( \nu_{\text{O-H},\text{products}} \) for the ionization of acetic acid is:

\[ \Delta \nu_{\text{O-H},\text{reactants}} = \nu_{\text{H},1} + \nu_{\text{H},2} + 5 \cdot (\nu_{\text{H},3}) \]  

(6.7)

\[ \Delta \nu_{\text{O-H},\text{products}} = 4 \cdot (\nu_{\text{H},4}) + 3 \cdot (\nu_{\text{H},5}) \]  

(6.8)
Five hydrogen bond stretching frequencies between water molecules, $\nu_{H,3}$, need to be broken in order to generate the four hydrogen bonds accepted by the acetate ion, $\nu_{H,4}$.

In their model, Bunton and Shiner used the approximation of Gordy and Stanford (1941) to estimate the stretching frequencies of hydrogen bonds, where Gordy and Stanford found linear relationships between the stretching frequencies of hydrogen-bonded species in aqueous solutions, and values of $pK_a$ ($\nu = 2937 + 28.8 \cdot pK_a$) and $pK_b$ ($\nu = 3040 + 22.9 \cdot pK_b$). Additional hydrogen bond stretching frequencies, attributed to hydrogen bonding between solvent molecules and the hydrogen bond between a solvent molecule and the hydroxyl oxygen atom were also considered. On the product side of the ionization reaction, two different types of stretching frequencies were considered. One type was attributed to hydrogen bonds between solvent molecules and the newly formed $H_3O^+$. The other type of stretching frequency was associated with hydrogen bonds between the solvent and the oxygen atoms on the now ionized acid. The predicted value of $\Delta pK_a$ of 0.50 for acetic acid from Bunton and Shiner (1961) at 298 K coincides well with the experimental value of 0.52 reported by Martin and Butler (1939).

Bunton and Shiner have shown that their model works very well at 298 K, where they have assumed that any long-range polarization effects within the solvent are negligible and that the Born equation (Born, 1920) does not have to be considered. We used equation (6.6) to calculate predicted values of $\Delta pK_{aq}$ as a function of temperature for CH$_3$COOD and D$_3$PO$_4$, by assuming that all hydrogen bond stretching frequencies are temperature independent and neglecting the long-range polarization solvent effects. The results are shown in Tables 6.1 and 6.2, respectively. Values of $pK_{a,CH_3COOH} = 4.74$, $pK_{b,CH_3COOH} = 20.2$ and $pK_{b,CH_3COO^-} = 9.26$ at $T = 298$ K, reported by Bunton and Shiner,
were used in Gordy and Stanford’s (1941) equations to estimate values of $\nu_{H,1}$, $\nu_{H,2}$ and $\nu_{H,4}$ ($\nu_{H,1} = 3074 \text{ cm}^{-1}$, $\nu_{H,2} = 3503 \text{ cm}^{-1}$, $\nu_{H,4} = 3259 \text{ cm}^{-1}$). The values of $\nu_{H,1}$, $\nu_{H,2}$ and $\nu_{H,4}$ were then used in equations (6.7) and (6.8). Values of $\nu_{H,3}$ and $\nu_{H,5}$ ($\nu_{H,3} = 3400 \text{ cm}^{-1}$ and $\nu_{H,5} = 2900 \text{ cm}^{-1}$) were also reported by Bunton and Shiner. Since equation (6.6) follows a simple inverse temperature relationship, with no consideration of how hydrogen bonding within the solvent changes as a function of temperature, it is likely that as temperature increases, the ability of equation (6.6) to accurately predict values of $\Delta pK_{aq}$ would decrease. This was found to be the case, where values of $\Delta pK_{aq}$ predicted by equation (6.6), at temperatures below 423 K, were found to be relatively close to the experimental values of $\Delta pK_{aq}$ reported in Chapter 3. However, at temperatures above, 423 K, it was found that equation (6.6) underestimated the isotope effect, up to 0.23 units in $\Delta pK_{aq}$.

Equation (6.6) was also used to estimate values of $\Delta pK_{aq}$ as a function of temperature for D$_3$PO$_4$. Figure 6.2, a modified version of Figure 1.20 for phosphoric acid, shows each of $\nu_{H,1}$ to $\nu_{H,5}$. In this figure, the co-ordination number of H$_2$O at 298 K is still four, represented by the stretching frequency $\nu_{H,1}$, and H$_2$O$^+$ still has a co-ordination number of three, represented by the stretching frequency $\nu_{H,5}$. Phosphoric acid has six hydrogen bonds to H$_2$O, represented by three $\nu_{H,1}$ and three $\nu_{H,2}$ stretching frequencies. $\nu_{H,1}$ corresponds to the H-O stretching frequency between one of the acidic protons and a neighboring H$_2$O molecule and $\nu_{H,2}$ corresponds to the O-H stretching frequency between a hydroxyl oxygen atom on the acid and a neighboring H$_2$O molecule.
Figure 6.2  The O-H stretching frequencies ($\nu_\text{H}$) observed on the reactants-side and products-side of the ionization reaction of phosphoric acid used to calculated values of $\Delta pK_{\text{aq}}$, using the method reported by Bunton and Shiner (1961). The dashed lines (- - - - - ) represent hydrogen bonds.
The dihydrogen phosphate anion still has two $\nu_{H,1}$ and two $\nu_{H,2}$ stretching frequencies, but it also has four $\nu_{H,4}$ stretching frequencies, corresponding to the hydrogen bonds between non-protonated oxygen atoms and neighboring H$_2$O molecules. Based on Figure 6.2, equations (6.7) and (6.8) are now modified for phosphoric acid as follows:

$$\Delta \nu_{O-H,\text{reactants}} = 3 \cdot (\nu_{H,1}) + 3 \cdot (\nu_{H,2}) + 5 \cdot (\nu_{H,3})$$

(6.9)

$$\Delta \nu_{O-H,\text{products}} = 2 \cdot (\nu_{H,1}) + 2 \cdot (\nu_{H,2}) + 4 \cdot (\nu_{H,4}) + 3 \cdot (\nu_{H,5})$$

(6.10)

In equation (6.9), five hydrogen bond stretching frequencies between water molecules, $\nu_{H,3}$, need to be broken to be accepted by the dihydrogen phosphate ion, $\nu_{H,4}$.

The value of $pK_{a,H_3PO_4} = 2.049$ at 298.174 K was taken from the experimental data reported in Chapter 4 and used to calculate $pK_{b,H_2PO_4^-} = 11.951$. These values were then used to calculate values of $\nu_{H,1}$ ($\nu_{H,1} = 2996$ cm$^{-1}$) and $\nu_{H,4}$ ($\nu_{H,4} = 3314$ cm$^{-1}$), using Gordy and Stanford’s (1941) equations. No known values of $pK_{b,H_3PO_4}$ have ever been reported in the literature. Therefore, using the method described by Paul and Long (1957), a value of $pK_{b,H_3PO_4}$ was estimated from a relationship between the Hammet acidity function value, $H_0$, for H$_3$PO$_4$, and a corresponding indicator acidity value, $pK_{BH^+}$:

$$H_0 = pK_{BH^+} - \log \left[ \frac{c_{BH^+}}{c_B} \right],$$

(6.11)

where $c_{BH^+}$ and $c_B$ are the concentrations of the indicator in its acidic and basic forms, respectively. The value of $pK_{BH^+}$, where $\log[c_{BH^+}/c_B]$ was equal to unity, has been reported by Lee and Stewart (1964). The subsequent value of $\nu_{H,2}$ was then calculated using Gordy and Stanford’s (1941) equation ($\nu_{H,2} = 3338$ cm$^{-1}$). The results shown in Table 6.2 indicate that at temperatures below 423 K, equations (6.6), (6.9) and (6.10) are
able to provide predicted values of $\Delta pK_{aq}$ for phosphoric acid, that agree reasonably well with those experimental values reported in Chapter 4. At temperatures above 423 K, however, equations (6.6), (6.9) and (6.10) are unable to accurately predict values of $\Delta pK_{aq}$.

Bunton and Shiner (1961) have shown that their model works well at 298 K for several species, but have not included the effects that temperature can have on hydrogen bonding. Therefore, to model values of $\Delta pK_{aq}$ as a function of temperature more accurately, we took into account the change in the coordination number of water as a function of temperature, as well as the effects of long-range polarization. Nakahara (2004) has reported that water has an average coordination number of approximately 4 at 298 K, which decreases to an average value of about 2.4 at 573 K. It has also been reported by Trevani et al. (2007) that isotope effects on long-range polarization can be estimated from the Born equation, using the dielectric constants of H$_2$O and D$_2$O.

Equations (6.7) and (6.8), for acetic acid, and equations (6.9) and (6.10), for phosphoric acid, were modified, by adjusting the value of the coefficient for each frequency, $\nu_{H1}$ to $\nu_{H5}$, at each temperature to represent a loss in the coordination number with increasing temperature:

$$\Delta \nu_{O-H,reactants} = c_1 \cdot (\nu_{H1}) + c_2 \cdot (\nu_{H2}) + c_3 \cdot (\nu_{H3})$$  \hspace{1cm} (6.12)

$$\Delta \nu_{O-H,products} = c_4 \cdot (\nu_{H1}) + c_5 \cdot (\nu_{H2}) + c_6 \cdot (\nu_{H4}) + c_7 \cdot (\nu_{H5})$$  \hspace{1cm} (6.13)

Here, $c_1$ to $c_7$ are the coefficients representing the average number of hydrogen-bonded stretching frequencies, $\nu_{H1}$ to $\nu_{H5}$, at each temperature. These values were estimated from the coordination number of H$_2$O as a function of temperature, reported by
Nakahara (2004), by assuming that at 298 K, the coefficients in front of $\nu_{1,1}$ to $\nu_{1,5}$ in equations (6.7) to (6.10) correctly represent the co-ordination numbers to each species at 298 K. This was done to maintain symmetry between the number of hydrogen bonds broken vs. the number of hydrogen bonds formed at each temperature. Values of $c_1$ to $c_7$ for acetic and phosphoric acid are reported in Tables 6.3 and 6.4, respectively, as a function of temperature. Tables 6.5 and 6.6 show the predicted values of $\Delta pK_{aq}$ for acetic and phosphoric acid, respectively, which were calculated using equations (6.12) and (6.13) in equation (6.6). These values were compared to the experimental values reported in Chapters 3 and 4. Also shown in Tables 6.5 and 6.6 are values for $\Delta pK_{aq}$ for acetic and phosphoric acid, predicted from equation (6.6) which were shown in Tables 6.1 and 6.2 above. By reducing the average number of hydrogen-bonds with increasing temperature, equation (6.6) becomes less effective at accurately predicting values of $\Delta pK_{aq}$ for both acetic and phosphoric acid with increasing temperature, when compared to Bunton and Shiner’s original equation. This trend is not surprising since, as temperature increases, long-range polarization effects within $\text{H}_2\text{O}$ become a more dominant factor in ion solvation. In considering only a change in co-ordination number as a function of temperature, long-range polarization effects have not been considered.

To develop the model further, we also decided to add on an additional factor to account for the isotope effect on the increase in long-range polarization with increasing temperature. This was done in the form of an empirical Born term, $\Delta \Delta_{\text{solv}}G_j^o$ (Born 1920; Shock et al., 1992):
Table 6.3. Values of the coefficients, $c_1$ to $c_7$, shown in equations (6.12) and (6.13), for acetic acid as a function of temperature.

<table>
<thead>
<tr>
<th>$T,\text{K}$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$c_4$</th>
<th>$c_5$</th>
<th>$c_6$</th>
<th>$c_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.85</td>
<td>1.00</td>
<td>1.00</td>
<td>5.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
<td>3.00</td>
</tr>
<tr>
<td>368.58</td>
<td>0.90</td>
<td>0.90</td>
<td>4.50</td>
<td>0.00</td>
<td>0.00</td>
<td>3.60</td>
<td>2.70</td>
</tr>
<tr>
<td>422.40</td>
<td>0.80</td>
<td>0.80</td>
<td>4.00</td>
<td>0.00</td>
<td>0.00</td>
<td>3.20</td>
<td>2.40</td>
</tr>
<tr>
<td>473.35</td>
<td>0.75</td>
<td>0.75</td>
<td>3.75</td>
<td>0.00</td>
<td>0.00</td>
<td>3.00</td>
<td>2.25</td>
</tr>
<tr>
<td>498.17</td>
<td>0.70</td>
<td>0.70</td>
<td>3.50</td>
<td>0.00</td>
<td>0.00</td>
<td>2.80</td>
<td>2.10</td>
</tr>
<tr>
<td>525.32</td>
<td>0.65</td>
<td>0.65</td>
<td>3.25</td>
<td>0.00</td>
<td>0.00</td>
<td>2.60</td>
<td>1.95</td>
</tr>
<tr>
<td>548.44</td>
<td>0.63</td>
<td>0.63</td>
<td>3.13</td>
<td>0.00</td>
<td>0.00</td>
<td>2.50</td>
<td>1.88</td>
</tr>
</tbody>
</table>
Table 6.4. Values of the coefficients, \( c_1 \) to \( c_7 \), shown in equations (6.12) and (6.13), for phosphoric acid as a function of temperature.

<table>
<thead>
<tr>
<th></th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
<th>( c_4 )</th>
<th>( c_5 )</th>
<th>( c_6 )</th>
<th>( c_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.17</td>
<td>3.00</td>
<td>3.00</td>
<td>5.00</td>
<td>2.00</td>
<td>2.00</td>
<td>4.00</td>
<td>3.00</td>
</tr>
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<td>374.22</td>
<td>2.70</td>
<td>2.70</td>
<td>4.50</td>
<td>1.80</td>
<td>1.80</td>
<td>3.60</td>
<td>2.70</td>
</tr>
<tr>
<td>423.30</td>
<td>2.40</td>
<td>2.40</td>
<td>4.00</td>
<td>1.60</td>
<td>1.60</td>
<td>3.20</td>
<td>2.40</td>
</tr>
<tr>
<td>471.88</td>
<td>2.25</td>
<td>2.25</td>
<td>3.75</td>
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<td>1.50</td>
<td>3.00</td>
<td>2.25</td>
</tr>
<tr>
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<td>2.10</td>
<td>2.10</td>
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<td>1.40</td>
<td>1.40</td>
<td>2.80</td>
<td>2.10</td>
</tr>
<tr>
<td>523.56</td>
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<td>1.95</td>
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<td>1.30</td>
<td>1.30</td>
<td>2.60</td>
<td>1.95</td>
</tr>
<tr>
<td>548.63</td>
<td>1.88</td>
<td>1.88</td>
<td>3.13</td>
<td>1.25</td>
<td>1.25</td>
<td>2.50</td>
<td>1.88</td>
</tr>
<tr>
<td>571.91</td>
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<td>1.80</td>
<td>3.00</td>
<td>1.20</td>
<td>1.20</td>
<td>2.40</td>
<td>1.80</td>
</tr>
</tbody>
</table>
Table 6.5. Comparison of experimental values of $\Delta pK_{\text{aq}}$ ($\Delta pK_{\text{aq,exp}}$) for acetic acid as a function of temperature, with predicted values of $\Delta pK_{\text{aq}}$ ($\Delta pK_{\text{aq,pred}}$)

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\Delta pK_{\text{aq,exp}}$</th>
<th>$\Delta pK_{\text{aq,pred}}^*$</th>
<th>$\Delta pK_{\text{aq,pred}}^{**}$</th>
<th>$\Delta pK_{\text{aq,pred}}^{***}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.85</td>
<td>0.52</td>
<td>0.50</td>
<td>0.50</td>
<td>0.51</td>
</tr>
<tr>
<td>368.58</td>
<td>0.43</td>
<td>0.40</td>
<td>0.36</td>
<td>0.38</td>
</tr>
<tr>
<td>422.40</td>
<td>0.44</td>
<td>0.35</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>473.35</td>
<td>0.45</td>
<td>0.32</td>
<td>0.24</td>
<td>0.26</td>
</tr>
<tr>
<td>498.17</td>
<td>0.49</td>
<td>0.30</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>525.32</td>
<td>0.45</td>
<td>0.28</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>548.44</td>
<td>0.50</td>
<td>0.27</td>
<td>0.17</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*Values predicted using equations (6.6) to (6.8), the method reported by Bunton and Shiner (1961)

**Values predicted using equation (6.6), (6.12) and (6.13)

***Values predicted using equation (6.12), (6.13) and (6.17)
Table 6.6.  Comparison of experimental values of $\Delta pK_{aq}$ ($\Delta pK_{aq, exp}$) for phosphoric acid as a function of temperature, with predicted values of $\Delta pK_{aq}$ ($\Delta pK_{aq, pred}$)

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\Delta pK_{aq, exp}$</th>
<th>$\Delta pK_{aq, pred}^*$</th>
<th>$\Delta pK_{aq, pred}^{**}$</th>
<th>$\Delta pK_{aq, pred}^{***}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.17</td>
<td>0.37</td>
<td>0.37</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>374.22</td>
<td>0.34</td>
<td>0.30</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>423.30</td>
<td>0.33</td>
<td>0.26</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>471.88</td>
<td>0.34</td>
<td>0.23</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>498.02</td>
<td>0.36</td>
<td>0.22</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>523.56</td>
<td>0.36</td>
<td>0.21</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>548.63</td>
<td>0.34</td>
<td>0.20</td>
<td>0.13</td>
<td>0.15</td>
</tr>
<tr>
<td>571.91</td>
<td>0.31</td>
<td>0.19</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Values predicted using equations (6.6), (6.9) and (6.10), the method reported by Bunton and Shiner (1961)

**Values predicted using equation (6.6), (6.12) and (6.13)

***Values predicted using equation (6.12), (6.13) and (6.17)
\[ \Delta \Delta_{\text{solv}} G_j^\circ = \Delta_{\text{solv,D}_2\text{O}} G_j^\circ - \Delta_{\text{solv,H}_2\text{O}} G_j^\circ \]

\[ = \frac{N \cdot e^2 \cdot z_j^2}{2 \cdot R_{e,j}} \left( \frac{1}{\varepsilon_{\text{D}_2\text{O}}} - \frac{1}{\varepsilon_{\text{H}_2\text{O}}} \right) \]  \hspace{1cm} (6.14)

Assuming that the electrostatic radius of the ion, \( R_{e,j} \), is constant in both solvents and as a function of temperature, equation (6.14) was derived using equation (1.17):

\[ \Delta_{\text{solv}} G_j^\circ = \frac{N \cdot e^2 \cdot z_j^2}{2 \cdot R_{e,j}} \left( \frac{1}{\varepsilon_{\text{D}_2\text{O}}} - 1 \right) \]  \hspace{1cm} (6.15)

where values of \( R_{e,j} \) for the acetate and phosphate anion were calculated from the values of \( R_{x,j} \), taken from Marcus (1994), according to equation (1.18):

\[ R_{e,j} = R_{x,j} + |Z_j| \cdot (k_z + g) \]  \hspace{1cm} (6.16)

The result was the following modified form of equation (6.6):

\[ \Delta pK_a = \sum v_{\text{O-H,reactants}} - \sum v_{\text{O-H,products}} \cdot \ln10 \cdot \Delta \Delta_{\text{solv}} G_j^\circ \]  \hspace{1cm} (6.17)

where \( v_{\text{O-H,reactants}} \) and \( v_{\text{O-H,products}} \) were calculated using equations (6.12) and (6.13).

Predicted values of \( \Delta pK_{aq} \) for acetic and phosphoric acid as a function of temperature, calculated using equation (6.17) are reported in Tables 6.5 and 6.6, respectively.

Addition of this Born term onto equation (6.6) to account for long-range polarization effects appears to slightly improve the predictive capability of equation (6.6) for values of \( \Delta pK_{aq} \) for acetic and phosphoric acid as a function of temperature.

### 6.2 Modelling \( \Delta pK_{aq} \) as a Function of \( pK_{aq,H_2O} \)

Additional studies using statistical mechanics have discussed that, besides the O-H stretching vibration, other factors need to be considered when predicting isotope effects.
Work by Stillinger and co-workers (Stillinger and Rahman, 1974; Stillinger et al., 1977) have discussed in great detail the importance of constructing and incorporating corrections into the classical dynamic interpretation of H₂O structure. Work by Bigeleisen (1960, 1961) on differences in vapour pressure as the result of isotopic substitution, has shown the importance of considering molecular structure in the statistical mechanic calculations of isotope effects. Marcus and Ben-Naim (1985) have echoed this work, stating the important role that solvent structure plays on isotope effects at temperatures removed from ambient conditions.

Experimentally, McDougall and Long (1962) and Salomaa and co-workers (Salomaa et al., 1964, 1969a, 1969b, 1969c) have investigated the effects of solvent medium on isotope effects on the ionization constants for weak acid systems. Plots of ΔpKₐ as a function of pKₐ,H₂O at 298 K, reported by these authors, have shown that as pKₐ,H₂O increases, corresponding values of ΔpKₐ also increase, but no simple relationship seems to exist. Their work has pointed out that the general increase in ΔpKₐ as a function of pKₐ,H₂O is expected, due to an increase in the zero-point energy associated with the strength of the O-H bond. However, the lack of a simple linear relationship indicates that in addition to considering the differences in zero-point energies when predicting values of ΔpKₐ, one must also consider the following: how isotope effects change the activity coefficient of the weak acid and its conjugate base, what the structural type of the acid in question is, and whether or not intramolecular hydrogen bonding occurs within the acid (McDougall and Long, 1962; Salomaa, 1969a). Perrin and Dong (2007) have also investigated how inductive effects and electron delocalization can affect values of ΔpKₐ.

The literature investigation of Laughton and Robertson (1969), has also shown that for
approximately 150 different weak acids, there is no simple linear trend when plotting \( \Delta pK_a \) as a function of \( pK_{H2O} \) at 298 K (Figure 1.17), providing further proof that isotope effects cannot simply be predicted from reduced mass calculations.

Mesmer and Herting (1978) investigated these plots of \( \Delta pK_a \) vs. \( pK_{a,H2O} \) as a function of temperature for \( D_2PO_4^- \), \( D_3PO_4 \), \( DSO_4^- \), \( DCO_3^- \) and \( D_2O \). The only known values of \( \Delta pK_a \) at temperatures greater than 373 K at the time were those of Shoesmith and Lee (1976), Mesmer and Herting (1978) for \( D_2PO_4^- \) and \( D_2O \) and Lietzke and Stoughton (1963) for \( DSO_4^- \). Mesmer and Herting postulated that if the isotope effect on \( \Delta pK_a \) with respect to \( pK_{a,H2O} \) was based on free energy, then plots of \( R \cdot T \cdot \log\left[\frac{K_{a,HA}}{K_{a,DA}}\right] \) vs. \( R \cdot T \cdot \log[K_{a,HA}] \) might show no temperature dependence and, upon investigation, they found this not to be true.

We have extended the approach for correlating \( \Delta pK_{aq} \) vs. \( pK_{aq,H2O} \) reported by Mesmer and Herting further, using more recent literature values. A plot of \( \Delta pK_{aq} \) as a function of \( pK_{aq,H2O} \) for \( D_3PO_4 \), \( D_2PO_4^- \), \( CH_3COOD \), \( DSO_4^- \), \( \beta \)-naphthol and B(OD)\(_3\), at 298 K, is shown below in Figure 6.3. Also, a plot of \( \Delta pK_{aq} \) as a function of \( pK_{aq,H2O} \) for \( D_3PO_4 \), \( D_2PO_4^- \), \( CH_3COOD \), \( \beta \)-naphthol and B(OD)\(_3\), at 548 K, is shown below in Figure 6.4 (Mesmer and Herting, 1978; Lietzke and Stoughton, 1963; Bulemela and Tremaine, 2009). Both these figures indicate that values of \( \Delta pK_{aq} \) generally tend to increase as a function of \( pK_{aq,H2O} \) at both temperatures, with the exception of the values reported by Bulemela and Tremaine (2009). By comparing the reported solid lines in Figures 6.3 and 6.4, we have confirmed the results reported by Mesmer and Herting, which indicate that the slope of \( \Delta pK_{aq} \) vs. \( pK_{aq,H2O} \) at 298 K is not the same as the slope at 548 K.
Figure 6.3 Correlation of values of $\Delta pK_{aq}$ for weak acids as a function of acid strength in $\text{H}_2\text{O}$ at 298 K: (●) $\text{D}_3\text{PO}_4$; (□) $\text{D}_2\text{PO}_4^-$ (Mesmer and Herting, 1978); (▲) $\text{CH}_3\text{COOD}$; (○)$\beta$-naphthol (Bulemela and Tremaine, 2009); (△) $\text{B(OD)}_3$ (Bulemela and Tremaine, 2009); and (△) $\text{DSO}_4^-$ (Lietzke and Stoughton, 1963). The solid line represents a line of best fit.
Figure 6.4  Correlation of values of $\Delta pK_{aq}$ for weak acids as a function of acid strength in H$_2$O at 548 K: (●) D$_3$PO$_4$; (□) D$_2$PO$_4^-$ (Mesmer and Herting, 1978); (▲) CH$_3$COOD; (●)β-naphthol (Bulemela and Tremaine, 2009); and (▽) B(OD)$_3$ (Bulemela and Tremaine, 2009). The solid line represents a line of best fit.
The scatter about the lines of best fit reported in Figures 6.3 and 6.4 also confirms the suggestions of Macdougall and Long (1938) and Salomaa et al. (1964, 1969a, 1969b, 1969c), that there is no simple relationship between $\Delta pK_{aq}$ and $pK_{aq,H2O}$, even at higher temperatures.

Other authors have used theoretical models and more pragmatic methods to correlate solvent isotope effects at high temperatures. Matsunaga et al. (1989) used the corresponding states principle (CSP) to correlate the viscosities of H$_2$O and D$_2$O up to near-critical temperatures. Van Hook et al. (2007) furthered this work by investigating liquid molar densities and vapor pressures of H$_2$O and D$_2$O to the critical point. Polyakov et al. (2007) have discussed the use of the compressibility factor, $Z$, to model ideal-gas like equations of state for H$_2^{18}$O in the low-density region of the solvent, and applied it to a three-parameter equation of state, allowing for calculations of the isotopic effects of critical parameters of H$_2$O and D$_2$O. Abdulkadirova et al. (2002) used the Krichevskii parameter, which has recently been discussed by Sedlbauer et al. (2000, 2004), to describe how the thermodynamic properties of D$_2$O, acting as a solute in H$_2$O, can be described as a function of temperature using the properties of pure H$_2$O. Trevani et al. (2007) have also shown that both the Born model and the corresponding states principle may be able to predict values of $\Delta pK_{aq}$ from differences in values of partial molal volumes. The quantitative data for $\Delta pK_{aq}$ from this thesis provides a basis for modeling solvent isotope effects using these approaches and more sophisticated methods so that we can eventually provide a better understanding of $\Delta pK_{aq}$ as a function of temperature up to and including the critical region.
CHAPTER 7
CONCLUSIONS AND FUTURE RESEARCH

7.1 Limiting Molar Conductivities in H₂O and D₂O Under Hydrothermal Conditions

Values of $\Lambda^\circ$ and have been measured for a wide variety of species in H₂O and D₂O under hydrothermal conditions, which have been reported in Chapters 3 and 4. Comparisons of values of $\Lambda^\circ$ for strong electrolytes in H₂O to previous literature values indicate that we have accurately measured these values of $\Lambda^\circ$, to within the combined experimental uncertainties. Comparisons of values of $\Lambda^\circ$ for strong electrolytes in D₂O to previous literature values (though not as available) also indicate that we have accurately measured these values of $\Lambda^\circ$, to within combined experimental uncertainties. The values of $\Lambda^\circ$ for the strong electrolytes in H₂O were used to calculate values of $\Lambda^\circ$ for acetic and phosphoric acid in H₂O, which were subsequently used to calculate values of $pK_{aq,H2O}$ for both species. Values of $\Lambda^\circ$ for the strong electrolytes in D₂O were used in a similar manner, in order to calculate values of $pK_{aq,D2O}$ for acetic and phosphoric acid, and finally values of $\Delta pK_{aq}$.

7.2 Isotope Effects on Ionization Constants Under Hydrothermal Conditions

Values of $pK_{aq}$ and $\Delta pK_{aq}$ have been measured for acetic acid (from $T = 368$ K to $T = 548$ K at $p = 20$ MPa), reported in Chapter 3, and for phosphoric acid (from $T = 298$ K to $T = 571$ K at $p = 20$ MPa), reported in Chapter 4. The measurements of values of $pK_{aq,H2O}$ have been proven to be accurate (by comparison to other values reported in the
literature), and the measurements of $pK_{aq,D2O}$ and $\Delta pK_{aq}$ are the first of their kind under hydrothermal conditions. Values of $pK_{a,H2O}$, $pK_{aq,D2O}$ and $\Delta pK_{aq}$ have also been successfully modeled for acetic and phosphoric acid by the density model to temperatures of $T = 371$ K.

Measurements of $\Delta pK_{aq}$ under hydrothermal conditions have shown trends similar to those seen previously in the literature. Values of $\Delta pK_{aq}$ at each elevated temperature, for both acetic and phosphoric acid, fall within the range of $\Delta pK_{aq} = 0.46 \pm 0.2$, the average values seen for species at $T = 298$ K. Values of $\Delta pK_{aq}$ for acetic acid at 298 K lies approximately 0.1 units higher than the value at 423 K, but values of $\Delta pK_{aq}$ tend to tend to swing up above 500 K. Values of $\Delta pK_{aq}$ for phosphoric acid, however, at $T = 298$ K, show more of a temperature insensitivity, when compared to the values measured under hydrothermal conditions.

### 7.3 Hydration Effects on Hydration Under Hydrothermal Conditions

Values of $\Lambda^\circ$ for the strong electrolytes in D$_2$O vs. H$_2$O were compared using the Walden product ratio, $R_{Walden}^{D/H}$, in Chapter 5, in order to investigate isotope effects on hydration under hydrothermal conditions. Values of $R_{Walden}^{D/H}$ for the salt solutions seemed to show a general trend: beginning at a value near unity at $T = 298$ K, then increasing as the temperature was increased and reaching a maximum value above unity at approximately $T = 423$ K, then decreasing (to values near or below unity) as the temperature was increased further, up to $T = 571$ K. These results were thought to be due to the “structure making” and “structure breaking” properties of the ions that dissociated from the salts, which caused the ion-localized solvent molecules to be either more or less
structured, when compared to the bulk solvent at $T = 298$ K. As the temperature increased, the secondary deuterium isotope effects became more noticeable, causing the mobility of the ions in D$_2$O vs. H$_2$O to differ, as was seen by values of $R_{\text{Walden}}^{\text{D/H}}$ that were no longer at or near unity. For DCl/HCl, NaOD/NaOH and KOD/KOH, values of $R_{\text{Walden}}^{\text{D/H}}$ increased with increasing temperature, approaching unity at $T = 571$ K. This trend has been attributed to the Grotthuss proton-hopping mechanism, which was thought to become more effective in D$_2$O vs. H$_2$O with increasing temperature, due to the temperature sensitivity of hydrogen bond strength, which is greater in D$_2$O vs. H$_2$O.

In order to look at the mobility of the ions in D$_2$O vs. H$_2$O, values of $\lambda^o$ were calculated from values of $\Lambda^o$ using transference numbers, $t^o$, that were either previously reported in the literature (for species in H$_2$O) or estimated from H$_2$O-based data (for species in D$_2$O). Values of $\lambda^o$ for the ions in D$_2$O vs. H$_2$O were compared, using $R_{\text{Walden}}^{\text{D/H}}$, as a function of temperature. The “structure breakers”: Cl$^-$, Na$^+$, CH$_3$COO$^-$ and D$_2$PO$_4^-$ /H$_2$PO$_4^-$, show trends similar to those discussed above for the salt solutions, where values of $R_{\text{Walden}}^{\text{D/H}}$ would start near unity at $T = 298$ K, increase and a reach a maximum value of $R_{\text{Walden}}^{\text{D/H}}$ above unity, then decrease to values of $R_{\text{Walden}}^{\text{D/H}}$ near or below unity, at temperatures up to $T = 571$ K. K$^+$, had a continued increase of $R_{\text{Walden}}^{\text{D/H}}$ as a function of temperature, starting at a value near unity at $T = 298$ K and increasing to a value near 1.13 at $T = 571$ K. The trend reported in this thesis supports the premise that K$^+$ is a “structure maker”. Values of $R_{\text{Walden}}^{\text{D/H}}$ for H$^+$/D$^+$ and OH$^-$/OD$^-$ started at values below unity at $T = 298$ K, and continued to increase to values approaching unity at $T = 571$ K. These trends were attributed to the Grotthuss mechanism.
7.4 Thesis Conclusions and Future Directions of Research

The experimental measurements of p$K_{\text{aq}}$ for CH$_3$COOD and D$_3$PO$_4$ are the first of their kind to be determined by conductivity measurements under hydrothermal conditions. Comparisons of experimental values of p$K_{\text{aq}}$ of CH$_3$COOH and H$_3$PO$_4$ with previous literature show a high degree of accuracy, demonstrating that AC conductivity is a powerful tool to measure degrees of ionization. Calculations of Walden product ratios as a function of temperature have been used to understand the differences in hydration effects of species in light and heavy water. The work presented in this thesis is the first step towards creating a predictive model for transition metal hydrolysis and oxide solubility in D$_2$O, from H$_2$O-based measurements. Currently Raman spectroscopy is being used to measure values of $\Delta pK_{\text{aq}}$ for bisulfate systems under hydrothermal conditions. More Raman measurements on carbonate systems and UV-Visible measurements on the other colorimetric indicators ($\beta$-naphthoic acid and acridine, see Appendix Figure A.1) could also provide further investigation into solvent isotope effects on ionization constants under hydrothermal conditions. There is currently more work being done on the investigation of hydration effects by exploring values of $R_{\text{Walden}}^{\text{D/H}}$ for Cs$^+$ and $\Gamma$, using the AC conductance cell, at temperatures up to $T = 573$ K. Other methods by which to calculate values of $\lambda^\circ$ from values of $t^\circ$ are also being investigated. Finally, further measurements of values of $\Delta V^\circ$ in D$_2$O vs. H$_2$O for strong electrolytes under hydrothermal conditions are planned, using the techniques discussed by Trevani et al. (2007). Such measurements can allow us to calculate values of $\Delta pK_{\text{aq}}$, using equations (1.10) to (1.15).
As more measurements on values of $\Delta pK_{aq}$ as a function of temperature are made, there will be more opportunities to model these effects using the methods of Mesmer and Herting (1978), Bunton and Shiner (1961). There will also be more opportunities to look at the trends of values of $\Delta pK_{aq}$ vs. $pK_{aq,H2O}$ under hydrothermal conditions, to see if any generalizations can be made. In future work, the density and HKF model can be used to model values of $\Delta pK_{aq}$ and $\Delta V^\circ$, respectively, in D$_2$O vs. H$_2$O as a function of temperature under hydrothermal conditions. The corresponding states principle can also be used to model values of $\Delta V^\circ$ in D$_2$O vs. H$_2$O near the critical point.
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APPENDIX A

Chapter 1
Figure A.1  $pK_a$ of $\text{H}_2\text{PO}_4^-$ (●), Mesmer and Herting (1978); $pK_a \pm 1$ of β-naphthol (□), Xiang and Johnston (1994); $pK_a$ of $\text{B(OH)}_3$ (▲), Mesmer et al. (1972); $pK_a$ of $\text{CH}_3\text{COOH}$ (■), Mesmer et al. (1989); $pK_a \pm 1$ of acridine (○), Ryan et al. (1997) and $pK_a \pm 1$ of β-naphthoic acid (◇), Xiang and Johnston (1997) as a function of $T$ (in $\text{H}_2\text{O}$) in order to depict the importance of measuring $\Delta pK_a$ values as a function of $T$. The figure is a repeat of one reported by Bulemela and Tremaine (2009).
Figure A.1 reports values of $pK_a$ for several species in H$_2$O under hydrothermal conditions. A colorimetric indicator (e.g., $\beta$-naphthol, $\beta$-napthoic acid, acridine) will have a calculated range where its $pK_a$ (±1) will overlap with the $pK_a$ of a buffer (e.g., H$_2$PO$_4^-$, B(OH)$_3$, CH$_3$COOH).
APPENDIX B

Chapter 2
Table B.1. Molalities of CH$_3$COOD (mol·kg$^{-1}$), integrated acetyl:methyl peak ratios, % impurities in D$_2$O, and calculated values of D$_2$O purity (%).

<table>
<thead>
<tr>
<th>$m_{CH3COOD}$ mol·kg$^{-1}$</th>
<th>Integrated peak (IP) ratio</th>
<th>% impurities</th>
<th>% D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67568</td>
<td>0.180</td>
<td>0.244</td>
<td>99.756</td>
</tr>
<tr>
<td>2.0564</td>
<td>0.060</td>
<td>0.247</td>
<td>99.753</td>
</tr>
<tr>
<td>8.3744</td>
<td>0.018</td>
<td>0.302</td>
<td>99.698</td>
</tr>
<tr>
<td>2.7374</td>
<td>0.048</td>
<td>0.263</td>
<td>99.737</td>
</tr>
<tr>
<td>2.9801</td>
<td>0.048</td>
<td>0.286</td>
<td>99.714</td>
</tr>
<tr>
<td>0.39218</td>
<td>0.330</td>
<td>0.259</td>
<td>99.741</td>
</tr>
<tr>
<td>2.0414</td>
<td>0.060</td>
<td>0.245</td>
<td>99.755</td>
</tr>
<tr>
<td>7.4829</td>
<td>0.021</td>
<td>0.315</td>
<td>99.685</td>
</tr>
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</table>
Table B.2. Molalities of KCl (mol·kg⁻¹), corresponding experimental values of $R_s$, predicted values of $k$ from Barthel et al., (1980) and Benson and Gordon (1945), and calculated $k_{cell}$ values at $T = 298.15$ K.

<table>
<thead>
<tr>
<th>$10^3 m_{KCl}$</th>
<th>$R_s$</th>
<th>$10^4 \kappa$</th>
<th>$k_{cell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol·kg⁻¹</td>
<td>Ω</td>
<td>S·cm⁻¹</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>1.6881</td>
<td>2609.2</td>
<td>3.8008</td>
<td>0.06502</td>
</tr>
<tr>
<td>5.9182</td>
<td>757.9</td>
<td>13.16</td>
<td>0.06481</td>
</tr>
<tr>
<td>12.769</td>
<td>355.3</td>
<td>28.11</td>
<td>0.06441</td>
</tr>
<tr>
<td>64.309</td>
<td>73.90</td>
<td>135.3</td>
<td>0.06505</td>
</tr>
<tr>
<td>95.367</td>
<td>50.71</td>
<td>197.2</td>
<td>0.06465</td>
</tr>
</tbody>
</table>
APPENDIX C

Chapter 3 – Part I
As mentioned in Section 3.1, the results and interpretations presented in Chapter 3 of this thesis have been previously reported in Erickson et al. (2011). After publication of these results, several errors were found within the Mathematica® subroutines I had designed for calculating the values of ΔpK_{aq}. In this section of Appendix C, a detailed account of these errors, as well as subsequent corrections will be discussed.

As discussed in Section 2.3.1, the calculation of Λ° for the strong electrolytes of HCl, NaAc and NaCl required an iterative process, according to equation (2.18):

$$
\Lambda = \Lambda^0 - S \cdot e^{1/2} + E \cdot c \cdot \ln[c] + J_1 \cdot c - J_2 \cdot c^{3/2}
$$

(C.1)

After the data had been reported in Erickson et al. (2011), it was discovered that the values of Λ° were not being calculated through an iterative process, rather just the initial estimate of Λ°, Λ_{trial}°. This correction was subsequently made in the Mathematica® subroutine, and values of Λ° reported in Tables 3.1 and 3.2 are now these corrected values. These corrected values have now also been used in equation (3.12):

$$
\log[Λ^0] = \log[A_1] + \left( A_2 + \frac{A_3}{\rho_w} \right) \cdot \log[η_w],
$$

(C.2)

to represent values of Λ° accurately as a function of solvent viscosity. The corrected values of the parameters A_1, A_2 and A_3 are reported in Table 3.4.

The Debye-Hückel parameters, A_{DH} and B_{DH}, used in the calculation of the mean ionic activity coefficient, γ±, were shown in equations (1.32) and (1.33):

$$
A_{DH} = \left( \frac{2 \cdot \pi \cdot N}{1000} \right)^{1/2} \cdot \frac{e^3}{(k_B \cdot \epsilon_{H_2O} \cdot T)^{3/2}} = \frac{4.2021 \cdot 10^6}{(\epsilon_{H_2O} \cdot T)^{3/2}}
$$

(C.3)

$$
B_{DH} = \left( \frac{8 \cdot \pi \cdot N \cdot e^3}{1000 \cdot k_B} \right)^{1/2} \cdot \frac{1}{(\epsilon_{H_2O} \cdot T)^{1/2}} = \frac{50.29 \cdot 10^8}{(\epsilon_{H_2O} \cdot T)^{1/2}},
$$

(C.4)
In equation (1.31):

$$\ln[\gamma_\pm] = \frac{-A_{DH} \cdot \sqrt{I}}{1 + (B_{DH} \cdot \hat{a}) \cdot \sqrt{I}},$$

(\text{C.5})

$\gamma_\pm$ is represented in a natural log function. Different literature sources, such as Stokes (1965), report equation (C.5) as a base-10 log function, resulting in different calculated values of $A_{DH}$ and $B_{DH}$. It was discovered after the results were reported in Erickson et al. (2011), that the form of equation (C.3) that was used in our Mathematica® subroutines was not consistent with equation (C.5), but was consistent for calculating $\gamma_\pm$ in a base-10 log function. This correction was subsequently made in the Mathematica® subroutine. Values of $pK_{aq}$ in H$_2$O and D$_2$O, and values of $\Delta pK_{aq}$ have now been corrected. These corrected values of $pK_{aq}$ and $\Delta pK_{aq}$ are now reported in Table 3.3.
Table C.1. Original values of experimental molar conductivities, $\Lambda^\text{exp}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for NaCl(aq), HAc(aq), NaAc(aq), HCl(aq), and NaOH(aq) in H$_2$O from $T = 368$ K to $T = 548$ K at $p = 20$ MPa, as reported by Erickson et al. (2011)

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^\text{exp}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>106.96 ± 0.15</td>
<td>103.69 ± 0.15</td>
<td>35.416 ± 0.019</td>
<td>341.54 ± 0.51</td>
<td>345.12 ± 0.51</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>126.95 ± 0.13</td>
<td>123.08 ± 0.13</td>
<td>26.794 ± 0.011</td>
<td>217.70 ± 0.23</td>
<td>777.2 ± 11.5</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>80.51 ± 0.12</td>
<td>78.05 ± 0.12</td>
<td>21.496 ± 0.0076</td>
<td>271.82 ± 0.38</td>
<td>274.89 ± 0.39</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>188.66 ± 0.57</td>
<td>182.90 ± 0.57</td>
<td>153.714 ± 0.062</td>
<td>840.4 ± 2.6</td>
<td>847.5 ± 2.6</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>164.9 ± 2.3</td>
<td>159.8 ± 2.3</td>
<td>90.885 ± 0.038</td>
<td>568.6 ± 8.2</td>
<td>575.2 ± 5.3</td>
</tr>
</tbody>
</table>

$T = (368.601 ± 0.045)$ K, $p = (17.5825 ± 0.0029)$ MPa

$k_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_w^\text{exp} = (1.4768 ± 0.0012) \cdot 10^{-6}$ S·cm$^{-1}$

$T = (422.40 ± 0.10)$ K, $p = (17.5023 ± 0.0035)$ MPa

$k_{\text{cell}} = (0.0629 ± 0.0017)$ cm$^{-1}$

$\kappa_w^\text{exp} = (2.7093 ± 0.0014) \cdot 10^{-6}$ S·cm$^{-1}$
Table C.1.  Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \times 10^6$</th>
<th>$c \times 10^6$</th>
<th>$\kappa_{corr} \times 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^o$</th>
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<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>193.74 ± 0.16</td>
<td>169.73 ± 0.16</td>
<td>113.64 ± 0.23</td>
<td>669.6 ± 1.5</td>
<td>678.5 ± 1.5</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>172.27 ± 0.13</td>
<td>150.92 ± 0.13</td>
<td>21.578 ± 0.027</td>
<td>142.98 ± 0.21</td>
<td>1173.7 ± 16.9</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>64.78 ± 0.13</td>
<td>56.75 ± 0.13</td>
<td>34.199 ± 0.030</td>
<td>591.5 ± 1.2</td>
<td>596.3 ± 1.2</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>157.92 ± 0.50</td>
<td>138.34 ± 0.50</td>
<td>172.237 ± 0.069</td>
<td>1245.0 ± 4.0</td>
<td>1255.9 ± 4.0</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>130.1 ± 1.8</td>
<td>114.0 ± 1.8</td>
<td>108.733 ± 0.038</td>
<td>953.9 ± 13.1</td>
<td>963.8 ± 13.2</td>
</tr>
</tbody>
</table>

$T = (473.35 \pm 0.12)$ K, $p = (17.5144 \pm 0.0044)$ MPa
$k_{cell} = (0.06482 \pm 0.00011)$ cm$^{-1}$
$\kappa_{w}^{exp} = (3.7682 \pm 0.0037) \times 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \times 10^6$</th>
<th>$c \times 10^6$</th>
<th>$\kappa_{corr} \times 10^6$</th>
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<th>$\Lambda^o$</th>
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<td></td>
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<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>1086.32 ± 0.16</td>
<td>922.94 ± 0.16</td>
<td>678.90 ± 3.10</td>
<td>735.6 ± 3.3</td>
<td>758.3 ± 3.4</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>9041.0 ± 1.2</td>
<td>7682.8 ± 1.2</td>
<td>135.36 ± 0.16</td>
<td>17.618 ± 0.021</td>
<td>1209.9 ± 18.0</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>582.373 ± 0.088</td>
<td>494.786 ± 0.088</td>
<td>313.30 ± 0.37</td>
<td>629.17 ± 0.76</td>
<td>645.42 ± 0.78</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>1654.3 ± 4.0</td>
<td>1405.5 ± 4.0</td>
<td>1806.7 ± 6.9</td>
<td>1285.4 ± 5.9</td>
<td>1322.8 ± 6.0</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>1332.6 ± 17.0</td>
<td>1132.2 ± 17.0</td>
<td>1121.5 ± 3.4</td>
<td>990.6 ± 13.2</td>
<td>1024.3 ± 13.7</td>
</tr>
</tbody>
</table>

$T = (498.17 \pm 0.10)$ K, $p = (20.8206 \pm 0.0046)$ MPa
$k_{cell} = (0.065088 \pm 0.000059)$ cm$^{-1}$
$\kappa_{w}^{exp} = (4.1109 \pm 0.0048) \times 10^{-6}$ S·cm$^{-1}$
Table C.1.  Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
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<tr>
<td></td>
<td>mol·kg⁻¹</td>
<td>mol·L⁻¹</td>
<td>S·cm⁻¹</td>
<td>S·cm²·mol⁻¹</td>
<td>S·cm²·mol⁻¹</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>112.13 ± 0.15</td>
<td>90.9 ± 0.15</td>
<td>77.65 ± 0.18</td>
<td>854.4 ± 2.2</td>
<td>863.0 ± 2.3</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>141.08 ± 0.13</td>
<td>114.3 ± 0.13</td>
<td>11.367 ± 0.021</td>
<td>99.57 ± 0.18</td>
<td>1253.2 ± 16.7</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>157.98 ± 0.14</td>
<td>128.04 ± 0.14</td>
<td>92.580 ± 0.080</td>
<td>731.64 ± 0.86</td>
<td>740.92 ± 0.87</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>202.25 ± 0.62</td>
<td>163.9 ± 0.62</td>
<td>222.91 ± 0.17</td>
<td>1359.9 ± 4.3</td>
<td>1375.3 ± 4.3</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>177.6 ± 2.4</td>
<td>144.0 ± 2.4</td>
<td>151.369 ± 0.069</td>
<td>1051.9 ± 14.3</td>
<td>1066.3 ± 14.5</td>
</tr>
</tbody>
</table>

$T = (525.32 ± 1.4)$ K, $p = (17.4945 ± 0.0026)$ MPa

$k_{cell} = (0.06501 ± 0.00077)$ cm⁻¹

$\kappa_w^{exp} = (4.4887 ± 0.0040) \cdot 10^{-6}$ S·cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>$m_{aq} \cdot 10^6$</th>
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<th>$\Lambda^{exp}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg⁻¹</td>
<td>mol·L⁻¹</td>
<td>S·cm⁻¹</td>
<td>S·cm²·mol⁻¹</td>
<td>S·cm²·mol⁻¹</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>1086.32 ± 0.16</td>
<td>846.46 ± 0.16</td>
<td>735.1 ± 1.5</td>
<td>868.4 ± 1.8</td>
<td>896.5 ± 1.9</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>904.11 ± 1.2</td>
<td>7047.4 ± 1.2</td>
<td>80.055 ± 0.048</td>
<td>11.3595 ± 0.0069</td>
<td>1292.7 ± 19.4</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>582.373 ± 0.088</td>
<td>453.784 ± 0.088</td>
<td>332.8 ± 1.3</td>
<td>736.1 ± 2.9</td>
<td>755.8 ± 3.0</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>1654.3 ± 4.0</td>
<td>1289.1 ± 4.0</td>
<td>1788.8 ± 6.7</td>
<td>1387.7 ± 6.2</td>
<td>1433.4 ± 6.4</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>1332.6 ± 17.0</td>
<td>1038.4 ± 17.0</td>
<td>1132.6 ± 4.6</td>
<td>1090.7 ± 14.9</td>
<td>1132.2 ± 15.4</td>
</tr>
</tbody>
</table>

$T = (548.44 ± 0.10)$ K, $p = (20.7406 ± 0.0079)$ MPa

$k_{cell} = (0.065055 ± 0.000059)$ cm⁻¹

$\kappa_w^{exp} = (4.4500 ± 0.0048) \cdot 10^{-6}$ S·cm⁻¹
Table C.2. Original values of experimental molar conductivities, $\Lambda^{\exp}$, and fitted limiting molar conductivities, $\Lambda^o$, for NaCl(aq), DAc(aq), NaAc(aq), DCl(aq), and NaOD(aq) in D$_2$O from $T = 368$ K to $T = 548$ K at $p = 20$ MPa, as reported by Erickson et al. (2011)

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>50.583 ± 0.087</td>
<td>48.948 ± 0.087</td>
<td>15.259 ± 0.014</td>
<td>311.73 ± 0.6</td>
<td>314.01 ± 0.61</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>612.11 ± 0.58</td>
<td>592.34 ± 0.58</td>
<td>29.952 ± 0.015</td>
<td>50.566 ± 0.054</td>
<td>579.3 ± 6.2</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>131.84 ± 0.13</td>
<td>127.58 ± 0.13</td>
<td>30.9123 ± 0.018</td>
<td>242.62 ± 0.28</td>
<td>246.27 ± 0.29</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>404.9 ± 1.6</td>
<td>391.18 ± 1.6</td>
<td>249.66 ± 0.32</td>
<td>637.2 ± 2.7</td>
<td>647.1 ± 2.4</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>181.0 ± 1.7</td>
<td>175.1 ± 1.7</td>
<td>63.422 ± 0.038</td>
<td>362.2 ± 3.5</td>
<td>368.8 ± 3.5</td>
</tr>
</tbody>
</table>

$T = (368.601 \pm 0.045)$ K, $p = (17.5825 \pm 0.0029)$ MPa

$k_{cell} = (0.0629 \pm 0.0017)$ cm$^{-1}$

$\kappa_w^{exp} = (5.1157 \pm 0.0042) \cdot 10^{-6}$ S·cm$^{-1}$

$T = (422.40 \pm 0.10)$ K, $p = (17.5023 \pm 0.0035)$ MPa

$k_{cell} = (0.0629 \pm 0.0017)$ cm$^{-1}$

$\kappa_w^{exp} = (8.2487 \pm 0.0058) \cdot 10^{-6}$ S·cm$^{-1}$
Table C.2. Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td>S·cm$^{-2}$·mol$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

$T = (473.35 \pm 0.12)$ K, $p = (17.5144 \pm 0.0044)$ MPa

$k_{cell} = (0.06482 \pm 0.00011)$ cm$^{-1}$

$\kappa_w^{exp} = (14.4543 \pm 0.0061) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl(aq)</td>
<td>117.26 ± 0.11</td>
<td>102.43 ± 0.11</td>
<td>55.641 ± 0.094</td>
<td>543.2 ± 1.0</td>
<td>549.6 ± 1.1</td>
</tr>
<tr>
<td>DAC(aq)</td>
<td>1092.92 ± 0.6</td>
<td>954.69 ± 0.60</td>
<td>29.427 ± 0.017</td>
<td>30.824 ± 0.025</td>
<td>1012.4 ± 9.7</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>220.41 ± 0.14</td>
<td>192.53 ± 0.14</td>
<td>101.89 ± 0.14</td>
<td>532.47 ± 0.81</td>
<td>540.82 ± 0.83</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>916.3 ± 3.0</td>
<td>800.4 ± 3.0</td>
<td>797.9 ± 1.3</td>
<td>996.9 ± 3.6</td>
<td>1021.3 ± 3.7</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>493.4 ± 4.2</td>
<td>431.0 ± 4.2</td>
<td>336.16 ± 0.21</td>
<td>779.9 ± 6.6</td>
<td>797.9 ± 6.8</td>
</tr>
</tbody>
</table>

$T = (498.17 ± 0.10)$ K, $p = (20.8206 ± 0.0046)$ MPa

$k_{cell} = (0.065088 ± 0.000059)$ cm$^{-1}$

$\kappa_w^{exp} = (14.947 ± 0.011) \cdot 10^{-6}$ S·cm$^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{aq} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{corr} \cdot 10^6$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl(aq)</td>
<td>744.116 ± 0.093</td>
<td>629.876 ± 0.093</td>
<td>352.7 ± 2.1</td>
<td>560.0 ± 3.3</td>
<td>577.6 ± 3.4</td>
</tr>
<tr>
<td>DAC(aq)</td>
<td>75825.5 ± 8.8</td>
<td>64297.1 ± 8.8</td>
<td>193.91 ± 0.14</td>
<td>3.0159 ± 0.0022</td>
<td>1042.0 ± 17.1</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>883.485 ± 0.098</td>
<td>747.870 ± 0.098</td>
<td>417.62 ± 0.52</td>
<td>564.89 ± 0.70</td>
<td>583.42 ± 0.72</td>
</tr>
<tr>
<td>DCI(aq)</td>
<td>4762.5 ± 13.0</td>
<td>4031.0 ± 13.0</td>
<td>3950.0 ± 47.9</td>
<td>979.8 ± 12.2</td>
<td>1036.3 ± 12.9</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>2531.3 ± 20.0</td>
<td>2142.7 ± 20.0</td>
<td>1634.6 ± 6.2</td>
<td>762.8 ± 6.7</td>
<td>805.8 ± 7.1</td>
</tr>
</tbody>
</table>
Table C.2. Continued

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^{\text{exp}}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>101.31 ± 0.11</td>
<td>81.74 ± 0.11</td>
<td>55.37 ± 0.10</td>
<td>677.5 ± 1.5</td>
<td>685.1 ± 1.5</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>566.24 ± 0.56</td>
<td>456.9 ± 0.56</td>
<td>11.898 ± 0.017</td>
<td>26.042 ± 0.025</td>
<td>1063.0 ± 9.9</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>173.54 ± 0.13</td>
<td>140.02 ± 0.13</td>
<td>84.39 ± 0.95</td>
<td>623.23 ± 0.61</td>
<td>632.32 ± 0.62</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>370.6 ± 1.4</td>
<td>299.0 ± 1.4</td>
<td>327.72 ± 0.28</td>
<td>1096.1 ± 4.4</td>
<td>1115.9 ± 4.4</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>390.5 ± 3.4</td>
<td>315.1 ± 3.4</td>
<td>273.97 ± 0.27</td>
<td>869.5 ± 7.6</td>
<td>889.7 ± 7.8</td>
</tr>
</tbody>
</table>

$T = (525.32 ± 1.4) \text{ K}, p = (17.4945 ± 0.0026) \text{ MPa}$

$k_{\text{cell}} = (0.06501 ± 0.00077) \text{ cm}^{-1}$

$\kappa_w^{\text{exp}} = (16.0201 ± 0.0047) \cdot 10^{-6} \text{ S·cm}^{-1}$

<table>
<thead>
<tr>
<th>Solute</th>
<th>$m_{\text{aq}} \cdot 10^6$</th>
<th>$c \cdot 10^6$</th>
<th>$\kappa_{\text{corr}} \cdot 10^6$</th>
<th>$\Lambda^{\text{exp}}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol·kg$^{-1}$</td>
<td>mol·L$^{-1}$</td>
<td>S·cm$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
<td>S·cm$^2$·mol$^{-1}$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>724.481 ± 0.093</td>
<td>561.430 ± 0.093</td>
<td>383.3 ± 2.1</td>
<td>682.7 ± 3.7</td>
<td>704.5 ± 3.8</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>75825.5 ± 8.8</td>
<td>58959.4 ± 8.8</td>
<td>117.703 ± 0.071</td>
<td>1.9963 ± 0.0012</td>
<td>1163.8 ± 13.7</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>883.485 ± 0.098</td>
<td>684.672 ± 0.098</td>
<td>416.2 ± 1.3</td>
<td>614.4 ± 1.9</td>
<td>637.1 ± 1.9</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>761.8 ± 2.5</td>
<td>590.4 ± 2.5</td>
<td>708.8 ± 1.7</td>
<td>1200.5 ± 4.9</td>
<td>1231.2 ± 5.1</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>2531.3 ± 20.0</td>
<td>1961.8 ± 2.0</td>
<td>1806.0 ± 6.8</td>
<td>920.6 ± 8.1</td>
<td>973.2 ± 8.6</td>
</tr>
</tbody>
</table>

$T = (548.44 ± 0.10) \text{ K}, p = (20.7406 ± 0.0079) \text{ MPa}$

$k_{\text{cell}} = (0.065055 ± 0.000059) \text{ cm}^{-1}$, $k_{\text{cell}} = (0.06477 ± 0.00011) \text{ cm}^{-1}$ (for DCl)

$k_w^{\text{exp}} = (15.3062 ± 0.0084) \cdot 10^{-6} \text{ S·cm}^{-1}$
Table C.3. Original calculated values of $K_{aq}$, $pK_{aq}$ and $\Delta pK_{aq}$ for HAc and DAc from $T = 368$ K to $T = 548$ K at $p = 20$ MPa, as reported by Erickson et al. (2011)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$K_{aq} \cdot 10^6$</th>
<th>$pK_{aq}$</th>
<th>$\Delta pK_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>368.601 ± 0.045</td>
<td>17.5825 ± 0.0029</td>
<td>13.93 ± 0.21</td>
<td>5.235 ± 0.057</td>
<td>4.8561 ± 0.0064</td>
</tr>
<tr>
<td>422.40 ± 0.10</td>
<td>17.5023 ± 0.0035</td>
<td>7.19 ± 0.11</td>
<td>2.667 ± 0.030</td>
<td>5.1431 ± 0.0061</td>
</tr>
<tr>
<td>473.35 ± 0.12</td>
<td>17.5144 ± 0.0044</td>
<td>2.950 ± 0.042</td>
<td>1.093 ± 0.010</td>
<td>5.5301 ± 0.0062</td>
</tr>
<tr>
<td>498.17 ± 0.10</td>
<td>20.8206 ± 0.0046</td>
<td>2.177 ± 0.034</td>
<td>0.807 ± 0.014</td>
<td>5.6622 ± 0.0064</td>
</tr>
<tr>
<td>525.32 ± 1.4</td>
<td>17.4945 ± 0.0026</td>
<td>0.980 ± 0.019</td>
<td>0.3626 ± 0.0036</td>
<td>6.009 ± 0.010</td>
</tr>
<tr>
<td>548.44 ± 0.10</td>
<td>20.7406 ± 0.0079</td>
<td>0.804 ± 0.012</td>
<td>0.2896 ± 0.0032</td>
<td>6.0948 ± 0.0065</td>
</tr>
</tbody>
</table>
APPENDIX C

Chapter 3 – Part II
Table C.4. Calculated Values for Parameters in Equivalent Circuit (Park et al., 2006) for NaCl(aq), HAc(aq), NaAc(aq), HCl(aq), and NaOH(aq) in H$_2$O from $T = 373$ K to $T = 548$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_w$</th>
<th>$C_T \cdot 10^{-4}$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.16</td>
<td>0.0428</td>
<td>42613.8 ± 35.1</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>5.67 ± 0.21</td>
<td>1.04 ± 0.12</td>
<td>1764.10 ± 0.89</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>6.06 ± 0.5</td>
<td>2.01 ± 0.52</td>
<td>2326.38 ± 0.81</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.62 ± 0.17</td>
<td>0.945 ± 0.093</td>
<td>2892.90 ± 0.84</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>6.79 ± 0.15</td>
<td>1.86 ± 0.13</td>
<td>408.72 ± 0.16</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>6.53 ± 0.23</td>
<td>1.94 ± 0.21</td>
<td>690.48 ± 0.28</td>
</tr>
</tbody>
</table>

$T = (368.601 ± 0.045)$ K, $p = (17.5825 ± 0.0029)$ MPa
$C_{cell} = (1.129 ± 0.0061) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0$ Ω

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_w$</th>
<th>$C_T \cdot 10^{-4}$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.16</td>
<td>0.0306</td>
<td>23215.1 ± 12.3</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>5.56 ± 0.21</td>
<td>1.12 ± 0.13</td>
<td>1175.22 ± 0.90</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>5.40 ± 0.47</td>
<td>3.8 ± 1.1</td>
<td>2420.15 ± 0.67</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.083 ± 0.091</td>
<td>1.625 ± 0.094</td>
<td>1826.83 ± 0.41</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>6.64 ± 0.19</td>
<td>2.45 ± 0.21</td>
<td>333.14 ± 0.17</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>6.71 ± 0.18</td>
<td>2.21 ± 0.18</td>
<td>538.63 ± 0.19</td>
</tr>
</tbody>
</table>

$T = (422.40 ± 0.10)$ K, $p = (17.5023 ± 0.0035)$ MPa
$C_{cell} = (0.9365 ± 0.0065) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0$ Ω
Table C.4. Continued.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_W$</th>
<th>$C_F \cdot 10^{-4}$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>F</td>
<td>Ω</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T = (473.35 \pm 0.12) \text{ K}, \ p = (17.5144 \pm 0.0044) \text{ MPa}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_{cell} = (0.601 \pm 0.015) \cdot 10^{-10} \text{ F}, \ C_D = 1 \cdot 10^{-10} \text{ F}, \ R_{ct} = 1.0 \text{ Ω}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.16</td>
<td>0.0304</td>
<td>17201.1 ± 16.9</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>5.84 ± 0.28</td>
<td>1.00 ± 0.15</td>
<td>557.9 ± 1.1</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>5.7 ± 2.0</td>
<td>3.1 ± 3.4</td>
<td>2686.5 ± 2.6</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.72 ± 0.44</td>
<td>1.49 ± 0.36</td>
<td>1763.9 ± 1.2</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>7.04 ± 0.17</td>
<td>2.07 ± 0.15</td>
<td>370.8 ± 0.14</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>7.22 ± 0.18</td>
<td>1.56 ± 0.12</td>
<td>582.47 ± 0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T = (498.17 \pm 0.10) \text{ K}, \ p = (20.8206 \pm 0.0046) \text{ MPa}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_{cell} = (0.545 \pm 0.019) \cdot 10^{-10} \text{ F}, \ C_D = 1 \cdot 10^{-10} \text{ F}, \ R_{ct} = 1.0 \text{ Ω}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.16</td>
<td>0.0189</td>
<td>15833.0 ± 18.6</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>6.42 ± 0.21</td>
<td>1.23 ± 0.12</td>
<td>95.46 ± 0.43</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>5.84 ± 0.25</td>
<td>2.46 ± 0.32</td>
<td>470.81 ± 0.52</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.37 ± 0.17</td>
<td>3.95 ± 0.40</td>
<td>205.85 ± 0.24</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>6.79 ± 0.20</td>
<td>2.90 ± 0.27</td>
<td>35.97 ± 0.14</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>7.27 ± 0.19</td>
<td>1.66 ± 0.14</td>
<td>57.89 ± 0.17</td>
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Table C.4.  Continued.

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</tr>
<tr>
<td>H$_2$O</td>
<td>3.16</td>
<td>0.0262</td>
<td>14482.3 ± 12.7</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>5.38 ± 0.34</td>
<td>1.11 ± 0.22</td>
<td>803.4 ± 1.7</td>
</tr>
<tr>
<td>HAc(aq)</td>
<td>15.8 ± 18.6</td>
<td>0.26 ± 0.84</td>
<td>4441.2 ± 5.10</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>6.57 ± 0.28</td>
<td>1.18 ± 0.16</td>
<td>678.22 ± 0.54</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>6.98 ± 0.29</td>
<td>2.51 ± 0.32</td>
<td>287.41 ± 0.21</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>7.27 ± 0.20</td>
<td>1.65 ± 0.14</td>
<td>420.38 ± 0.18</td>
</tr>
</tbody>
</table>

$T = (525.32 \pm 1.4)$ K, $p = (17.4945 \pm 0.0026)$ MPa

$C_{cell} = (0.655 \pm 0.016) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0 \Omega$

|          |             |                      |       |       |
|----------|-------------|----------------------|-------|
|          |             |                      |       |       |
|          |             |                      |       |       |
| H$_2$O   | 3.16        | 0.0149               | 14619.0 ± 15.9 |
| NaCl(aq) | 6.50 ± 0.15 | 1.93 ± 0.13          | 88.11 ± 0.18  |
| HAc(aq)  | 3.36 ± 0.61 | 81.0 ± 49.0          | 781.10 ± 0.40 |
| NaAc(aq) | 5.93 ± 0.58 | 3.7 ± 1.1            | 193.61 ± 0.76 |
| HCl(aq)  | 6.96 ± 0.31 | 5.46 ± 0.73          | 36.30 ± 0.14  |
| NaOH(aq) | 6.76 ± 0.19 | 1.65 ± 0.14          | 57.27 ± 0.23  |

$T = (548.44 \pm 0.10)$ K, $p = (20.7406 \pm 0.0079)$ MPa

$C_{cell} = (0.413 \pm 0.018) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0 \Omega$
Table C.5. Calculated Values for Parameters in Equivalent Circuit (Park et al., 2006) for NaCl(aq), DAc(aq), NaAc(aq), DCl(aq), and NaOD(aq) in D$_2$O from $T = 373$ K to $T = 548$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_W$</th>
<th>$C_f \cdot 10^{-4}$</th>
<th>$R_s$</th>
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<td>F</td>
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<tr>
<td>$T = (368.601 \pm 0.045)$ K, $p = (17.5825 \pm 0.0029)$ MPa</td>
<td></td>
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</tr>
<tr>
<td>$C_{cell} = (1.111 \pm 0.017) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0$ Ω</td>
<td></td>
<td></td>
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<tr>
<td>D$_2$O</td>
<td>3.16</td>
<td>0.0255</td>
<td>12301.6 ± 10.0</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>5.20 ± 0.34</td>
<td>1.32 ± 0.27</td>
<td>3285.4 ± 1.7</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>6.09 ± 0.36</td>
<td>1.92 ± 0.36</td>
<td>1859.23 ± 0.60</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.43 ± 0.17</td>
<td>1.25 ± 0.12</td>
<td>1807.93 ± 0.71</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>6.84 ± 0.22</td>
<td>1.87 ± 0.18</td>
<td>248.20 ± 0.31</td>
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<tr>
<td>NaOD(aq)</td>
<td>6.07 ± 0.31</td>
<td>2.19 ± 0.35</td>
<td>934.84 ± 0.47</td>
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<tr>
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<tr>
<td>$T = (422.40 \pm 0.10)$ K, $p = (17.5023 \pm 0.0035)$ MPa</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$C_{cell} = (0.946 \pm 0.022) \cdot 10^{-10}$ F, $C_D = 1 \cdot 10^{-10}$ F, $R_{ct} = 1.0$ Ω</td>
<td></td>
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<tr>
<td>D$_2$O</td>
<td>3.16</td>
<td>0.0221</td>
<td>7625.1 ± 5.4</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>4.97 ± 0.30</td>
<td>1.76 ± 0.34</td>
<td>2161.6 ± 1.4</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>6.06 ± 0.28</td>
<td>2.37 ± 0.35</td>
<td>1815.09 ± 0.39</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.29 ± 0.22</td>
<td>1.65 ± 0.22</td>
<td>1129.59 ± 0.79</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>6.84 ± 0.15</td>
<td>2.13 ± 0.14</td>
<td>198.77 ± 0.14</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>6.32 ± 0.22</td>
<td>2.29 ± 0.25</td>
<td>677.63 ± 0.26</td>
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Table C.5. Continued.

<table>
<thead>
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<th>$R_s \Omega$</th>
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</tr>
<tr>
<td></td>
<td></td>
<td>$F$</td>
<td>$\Omega$</td>
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</tbody>
</table>

$T = (473.35 \pm 0.12) \text{ K}, \ p = (17.5144 \pm 0.0044) \text{ MPa}$

$C_{\text{cell}} = (0.767 \pm 0.023) \cdot 10^{-10} \text{ F}, \ C_D = 1 \cdot 10^{-10} \text{ F}, \ R_{ct} = 1.0 \text{ $\Omega$}$

<p>| | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>D$_2$O</td>
<td>3.16</td>
<td>0.0833</td>
<td>4484.4</td>
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<tr>
<td>NaCl(aq)</td>
<td>5.07 ± 0.32</td>
<td>1.950 ± 0.40</td>
<td>941.1 ± 1.2</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>5.65 ± 0.42</td>
<td>4.7 ± 1.1</td>
<td>1519.32 ± 0.40</td>
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<tr>
<td>NaAc(aq)</td>
<td>5.07 ± 0.25</td>
<td>2.75 ± 0.43</td>
<td>563.04 ± 0.66</td>
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<tr>
<td>DCl(aq)</td>
<td>7.29 ± 0.17</td>
<td>2.11 ± 0.16</td>
<td>79.91 ± 0.12</td>
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<tr>
<td>NaOD(aq)</td>
<td>7.46 ± 0.13</td>
<td>1.638 ± 0.089</td>
<td>185.52 ± 0.11</td>
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</table>

$T = (498.17 \pm 0.10) \text{ K}, \ p = (20.8206 \pm 0.0046) \text{ MPa}$

$C_{\text{cell}} = (0.740 \pm 0.045) \cdot 10^{-10} \text{ F}, \ C_D = 1 \cdot 10^{-10} \text{ F}, \ R_{ct} = 1.0 \text{ $\Omega$}$

<p>| | | | |</p>
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<tr>
<td>D$_2$O</td>
<td>3.16</td>
<td>0.0649</td>
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<td>NaCl(aq)</td>
<td>5.53 ± 0.34</td>
<td>1.69 ± 0.33</td>
<td>177.61 ± 0.99</td>
</tr>
<tr>
<td>DAc(aq)</td>
<td>6.82 ± 0.13</td>
<td>1.241 ± 0.071</td>
<td>313.46 ± 0.20</td>
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<td>NaAc(aq)</td>
<td>5.52 ± 0.14</td>
<td>3.97 ± 0.32</td>
<td>150.90 ± 0.18</td>
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<tr>
<td>DCl(aq)</td>
<td>5.08 ± 0.36</td>
<td>17.6 ± 3.9</td>
<td>16.42 ± 0.20</td>
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<tr>
<td>NaOD(aq)</td>
<td>7.41 ± 0.16</td>
<td>1.54 ± 0.11</td>
<td>39.49 ± 0.15</td>
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</table>
### Table C.5. Continued.

<table>
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<th>System</th>
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<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$T = (525.32 \pm 1.4) \text{ K}, p = (17.4945 \pm 0.0026) \text{ MPa}$

$C_{cell} = (0.631 \pm 0.017) \cdot 10^{-10} \text{ F}, C_D = 1 \cdot 10^{-10} \text{ F}, R_{ct} = 1.0 \Omega $

<table>
<thead>
<tr>
<th></th>
<th>$C_I \cdot 10^{-4}$</th>
<th>$R_s$</th>
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<tbody>
<tr>
<td>$D_2O$</td>
<td>3.16</td>
<td>0.0886</td>
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<tr>
<td>NaCl(aq)</td>
<td>5.67 ± 0.48</td>
<td>1.66 ± 0.45</td>
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<tr>
<td>DaC(aq)</td>
<td>10.4 ± 3.1</td>
<td>0.94 ± 0.81</td>
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<tr>
<td>NaAc(aq)</td>
<td>5.84 ± 0.37</td>
<td>2.39 ± 0.47</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>6.98 ± 0.19</td>
<td>2.11 ± 0.17</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>7.46 ± 0.81</td>
<td>2.47 ± 0.93</td>
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</table>

$T = (548.44 \pm 0.10) \text{ K}, p = (20.7406 \pm 0.0079) \text{ MPa}$

$C_{cell} = (0.609 \pm 0.031) \cdot 10^{-10} \text{ F}, C_D = 1 \cdot 10^{-10} \text{ F}, R_{ct} = 1.0 \Omega $

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<th>$R_s$</th>
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</thead>
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<td>$D_2O$</td>
<td>3.16</td>
<td>0.0987</td>
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<td>NaCl(aq)</td>
<td>5.51 ± 0.33</td>
<td>1.89 ± 0.36</td>
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<tr>
<td>DaC(aq)</td>
<td>5.2 ± 1.4</td>
<td>38.8 ± 33.6</td>
</tr>
<tr>
<td>NaAc(aq)</td>
<td>5.60 ± 0.23</td>
<td>2.48 ± 0.33</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>7.08 ± 0.31</td>
<td>3.24 ± 0.42</td>
</tr>
<tr>
<td>NaOD(aq)</td>
<td>6.77 ± 0.12</td>
<td>1.87 ± 0.11</td>
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</table>
Table C.6. Values of $\rho$ and $\rho_{\text{H}_2\text{O}}$ for each solution in H$_2$O at each of the temperature and pressure conditions reported in Chapter 3.

<table>
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<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho_{\text{H}_2\text{O}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{NaCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{CH}_3\text{COOH}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{CH}_3\text{COONa}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{HCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{NaOH}}$ (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>368.601</td>
<td>17.5825</td>
<td>0.969505</td>
<td>0.969509</td>
<td>0.969506</td>
<td>0.969508</td>
<td>0.969509</td>
<td>0.969512</td>
</tr>
<tr>
<td>422.40</td>
<td>17.5023</td>
<td>0.927038</td>
<td>0.927043</td>
<td>0.927039</td>
<td>0.927042</td>
<td>0.927042</td>
<td>0.927045</td>
</tr>
<tr>
<td>473.35</td>
<td>17.5144</td>
<td>0.876041</td>
<td>0.876050</td>
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<td>0.876045</td>
<td>0.876047</td>
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<tr>
<td>498.17</td>
<td>20.8206</td>
<td>0.849583</td>
<td>0.849639</td>
<td>0.849670</td>
<td>0.849615</td>
<td>0.849636</td>
<td>0.849654</td>
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<tr>
<td>525.32</td>
<td>17.4945</td>
<td>0.810491</td>
<td>0.810498</td>
<td>0.810493</td>
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<td>0.810499</td>
<td>0.810502</td>
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<td>548.44</td>
<td>20.7406</td>
<td>0.779169</td>
<td>0.779242</td>
<td>0.779259</td>
<td>0.779210</td>
<td>0.779245</td>
<td>0.779262</td>
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Table C.7. Values of $\rho$ and $\rho_{\text{D}_2\text{O}}$ for each solution in D$_2$O at each of the temperature and pressure conditions reported in Chapter 3.

<table>
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<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho_{\text{D}_2\text{O}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{NaCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{CH}_3\text{COOH}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{CH}_3\text{COONa}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{DCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{NaOD}}$ (g·cm$^{-3}$)</th>
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<td>368.601</td>
<td>17.5825</td>
<td>1.075789</td>
<td>1.075790</td>
<td>1.075790</td>
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<td>1.075800</td>
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<td>1.028550</td>
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<tr>
<td>473.35</td>
<td>17.5144</td>
<td>0.971085</td>
<td>0.971091</td>
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<td>0.971096</td>
<td>0.971111</td>
<td>0.971110</td>
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<td>498.17</td>
<td>20.8206</td>
<td>0.941020</td>
<td>0.941059</td>
<td>0.941453</td>
<td>0.941067</td>
<td>0.941175</td>
<td>0.941161</td>
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<td>17.4945</td>
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<td>0.861518</td>
<td>0.861668</td>
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Table C.8. Values of $V^\circ$ for Na$^+$, Cl$^-$, CH$_3$COOH, CH$_3$COO$^-$ and OH$^-$ in H$_2$O at each of the temperature and pressure conditions reported in Chapter 3, obtained from SUPCRT (Johnson et al. 1992).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$V_{Na^+}^\circ$ (cm$^3$·mol$^{-1}$)</th>
<th>$V_{Cl^-}^\circ$ (cm$^3$·mol$^{-1}$)</th>
<th>$V_{CH_3COOH}^\circ$ (cm$^3$·mol$^{-1}$)</th>
<th>$V_{CH_3COO^-}^\circ$ (cm$^3$·mol$^{-1}$)</th>
<th>$V_{OH^-}^\circ$ (cm$^3$·mol$^{-1}$)</th>
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<tbody>
<tr>
<td>368.601</td>
<td>17.5825</td>
<td>0.9</td>
<td>16.6</td>
<td>54.6</td>
<td>38.9</td>
<td>-4.3</td>
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<td>422.40</td>
<td>17.5023</td>
<td>0.5</td>
<td>12.7</td>
<td>55.8</td>
<td>35.3</td>
<td>-8.7</td>
</tr>
<tr>
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<td>17.5144</td>
<td>-0.9</td>
<td>4.9</td>
<td>57.0</td>
<td>28.2</td>
<td>-17.6</td>
</tr>
<tr>
<td>498.17</td>
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<td>-1.1</td>
<td>57.8</td>
<td>22.5</td>
<td>-24.4</td>
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<td>17.4945</td>
<td>-4.5</td>
<td>-13.8</td>
<td>59.5</td>
<td>10.9</td>
<td>-38.9</td>
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<td>-29.0</td>
<td>61.3</td>
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<td>-55.9</td>
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Table C.9. Values of $\rho$, $\eta$ and $\varepsilon$ for H$_2$O and D$_2$O at each of the temperature and pressure conditions reported in Chapter 3.

<table>
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<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\eta$</th>
<th>$\varepsilon$</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\eta$</th>
<th>$\varepsilon$</th>
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</thead>
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<td>17.5825</td>
<td>0.969505</td>
<td>0.003006</td>
<td>57.31</td>
<td>1.075789</td>
<td>0.003520</td>
<td>57.08</td>
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<td>0.927038</td>
<td>0.001877</td>
<td>44.81</td>
<td>1.028536</td>
<td>0.002168</td>
<td>44.61</td>
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<td>17.5144</td>
<td>0.876041</td>
<td>0.001381</td>
<td>35.38</td>
<td>0.971085</td>
<td>0.001566</td>
<td>35.23</td>
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<td>0.849583</td>
<td>0.001233</td>
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<td>0.941020</td>
<td>0.001385</td>
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<td>0.810491</td>
<td>0.001088</td>
<td>27.43</td>
<td>0.896942</td>
<td>0.001210</td>
<td>27.32</td>
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<td>548.44</td>
<td>20.7406</td>
<td>0.779169</td>
<td>0.000998</td>
<td>24.43</td>
<td>0.861481</td>
<td>0.001102</td>
<td>24.33</td>
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</table>
Table C.10. Values of hydrolysis constants (Johnson et al., 1992), log $K_h$, for equation (3.8), corresponding degree of hydrolysis, $\alpha_{\text{hyd}}$, experimental aquamolalities, $m_{\text{aq}}$, corrected aquamolalities, $m_{\text{aq,eq}}$, molar conductivities, $\Lambda^\text{exp}$, corrected molar conductivities, $\Lambda^\text{exp,eq}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for NaAc(aq) in H$_2$O and corrected aquamolalities and corrected molar conductivities for NaOH(aq) in H$_2$O from $T = 368$ K to $T = 548$ K at $p = 20$ MPa

| $T^*$ (K) | $p^*$ (MPa) | log $K_h$ | $\alpha_{\text{hyd}}$ | NaOH(aq) | | | | | | | | NaAc(aq) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 368.60 | 17.5825 | -7.383 | 0.022 | 1.81 ± 0.12 | 429.52 ± 0.38 | | 80.51 | 78.70 | 275.41 | 271.87 | 274.15 |
| 422.40 | 17.5023 | -6.426 | 0.060 | 5.31 ± 0.12 | 545.82 ± 0.60 | | 80.51 | 75.20 | 441.35 | 433.97 | 437.77 |
| 473.35 | 17.5144 | -5.734 | 0.155 | 10.05 ± 0.13 | 662.04 ± 0.57 | | 64.78 | 54.73 | 602.6 | 590.9 | 595.6 |
| 498.17 | 20.8206 | -5.447 | 0.075 | 43.863 ± 0.088 | 680.17 ± 0.76 | | 582.37 | 538.50 | 633.22 | 629.40 | 647.18 |
| 525.32 | 17.4945 | -5.175 | 0.178 | 28.09 ± 0.14 | 682.51 ± 0.57 | | 157.98 | 129.89 | 723.04 | 731.26 | 741.38 |
| 548.44 | 20.7406 | -4.958 | 0.128 | 74.775 ± 0.088 | 713.68 ± 2.9 | | 582.37 | 507.59 | 733.4 | 736.3 | 757.8 |

*Corresponding uncertainties are reported in Table 3.1
Table C.11. Values of hydrolysis constants (Johnson et al., 1992), \( \log K_h \), for equation (3.8), corresponding degree of hydrolysis, \( \alpha_{hyd} \), experimental aquamolalities, \( m_{aq} \), corrected aquamolalities, \( m_{aq,eq} \), molar conductivities, \( \Lambda^{exp} \), corrected molar conductivities, \( \Lambda^{exp,eq} \), and fitted limiting molar conductivities, \( \Lambda^o \) for NaAc(aq) in D\(_2\)O and corrected aquamolalities and corrected molar conductivities for NaOD(aq) in D\(_2\)O from \( T = 368 \) K to \( T = 548 \) K at \( p = 20 \) MPa.

<table>
<thead>
<tr>
<th>( T^* ) (K)</th>
<th>( p^* ) (MPa)</th>
<th>( \log K_h )</th>
<th>( \alpha_{hyd} )</th>
<th>( m_{aq,c} \cdot 10^6 )</th>
<th>( \Lambda^{exp,eq} )</th>
<th>( m_{aq} \cdot 10^6 )</th>
<th>( m_{aq,eq} \cdot 10^6 )</th>
<th>( \Lambda^{exp} )</th>
<th>( \Lambda^{exp,eq} )</th>
<th>( \Lambda^o )</th>
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<tbody>
<tr>
<td>368.601</td>
<td>17.5825</td>
<td>-7.383</td>
<td>0.205</td>
<td>2.44 ± 0.13</td>
<td>222.27 ± 0.28</td>
<td>131.84</td>
<td>129.40</td>
<td>242.30</td>
<td>242.68</td>
<td>245.21</td>
</tr>
<tr>
<td>422.40</td>
<td>17.5023</td>
<td>-6.426</td>
<td>0.235</td>
<td>7.21 ± 0.13</td>
<td>302.89 ± 0.56</td>
<td>131.84</td>
<td>124.63</td>
<td>398.87</td>
<td>404.43</td>
<td>408.77</td>
</tr>
<tr>
<td>473.35</td>
<td>17.5144</td>
<td>-5.734</td>
<td>0.265</td>
<td>20.26 ± 0.14</td>
<td>493.42 ± 0.81</td>
<td>220.41</td>
<td>200.15</td>
<td>529.20</td>
<td>532.99</td>
<td>541.00</td>
</tr>
<tr>
<td>498.17</td>
<td>20.8206</td>
<td>-5.447</td>
<td>0.243</td>
<td>57.284 ± 0.098</td>
<td>456.68 ± 0.70</td>
<td>883.485</td>
<td>826.190</td>
<td>558.42</td>
<td>565.47</td>
<td>583.81</td>
</tr>
<tr>
<td>525.32</td>
<td>17.4945</td>
<td>-5.175</td>
<td>0.177</td>
<td>32.39 ± 0.13</td>
<td>504.34 ± 0.61</td>
<td>173.54</td>
<td>142.89</td>
<td>602.75</td>
<td>625.34</td>
<td>635.24</td>
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<tr>
<td>548.44</td>
<td>20.7406</td>
<td>-4.958</td>
<td>0.281</td>
<td>98.071 ± 0.098</td>
<td>550.6 ± 1.9</td>
<td>883.485</td>
<td>785.403</td>
<td>608.0</td>
<td>615.1</td>
<td>640.1</td>
</tr>
</tbody>
</table>

*Corresponding uncertainties in the temperature and pressure are reported in Table 3.2.
Figure C.1. Comparison of experimental (●) and predicted (—) impedance data for a) H$_2$O, and b) D$_2$O at $T = 368.60$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $Z_{im} = 0$. 
Figure C.2. Comparison of experimental (●) and predicted (——) impedance data for a) NaCl in H₂O, and b) NaCl in D₂O at $T = 368.60$ K. The dotted line (‘...’) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.3. Comparison of experimental (●) and predicted (——) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 368.60$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $Z_{\text{Im}} = 0$. 

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Figure C.4. Comparison of experimental (●) and predicted (—) impedance data for a) NaCH₃COO in H₂O, and b) NaCH₃COO in D₂O at $T = 368.60$ K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to $Z_{\text{Im}} = 0$. 
Figure C.5. Comparison of experimental (●) and predicted (—) impedance data for a) HCl in H₂O, and b) DCl in D₂O at \( T = 368.60 \) K. The dotted line (･･･) shows the extrapolated real resistance, the white point (○), to \( Z_{Im} = 0 \).
Figure C.6. Comparison of experimental (●) and predicted (—) impedance data for a) NaOH in H₂O, and b) NaOD in D₂O at $T = 368.60$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.7. Comparison of experimental (●) and predicted (---) impedance data for a) H₂O, and b) D₂O at $T = 422.40$ K. The dotted line (' . . . ') shows the extrapolated real resistance, the white point (⊙), to $Z_{lm} = 0$. 
Figure C.8. Comparison of experimental (●) and predicted (——) impedance data for a) NaCl in H$_2$O, and b) NaCl in D$_2$O at $T = 422.40$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $Z_{im} = 0$. 
Figure C.9. Comparison of experimental (●) and predicted (——) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 422.40$ K. The dotted line (‘.’) shows the extrapolated real resistance, the white point (⊙), to $Z_{im} = 0$. 
Figure C.10. Comparison of experimental (●) and predicted (—) impedance data for a) NaCH$_3$COO in H$_2$O, and b) NaCH$_3$COO in D$_2$O at $T = 422.40$ K. The dotted line (‘···’) shows the extrapolated real resistance, the white point (⊙), to $Z_{im} = 0$. 
Figure C.11. Comparison of experimental (●) and predicted (—) impedance data for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 422.40$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $Z_{lm} = 0$. 
Figure C.12. Comparison of experimental (●) and predicted (---) impedance data for a) NaOH in H₂O, and b) NaOD in D₂O at \( T = 422.40 \) K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to \( Z_{im} = 0 \).
Figure C.13. Comparison of experimental (●) and predicted (—) impedance data for a) H₂O, and b) D₂O at $T = 473.35$ K. The dotted line (⋯) shows the extrapolated real resistance, the white point (○), to $Z_{im} = 0$. 
Figure C.14. Comparison of experimental (●) and predicted (——) impedance data for a) NaCl in H$_2$O, and b) NaCl in D$_2$O at $T = 473.35$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 

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Figure C.15. Comparison of experimental (●) and predicted (——) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 473.35$ K. The dotted line (′′′′) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 

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Figure C.16. Comparison of experimental (●) and predicted (---) impedance data for a) NaCH$_3$COO in H$_2$O, and b) NaCH$_3$COO in D$_2$O at $T = 473.35$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.17. Comparison of experimental (●) and predicted (—) impedance data for a) HCl in H$_2$O, and b) DCl in D$_2$O at \( T = 473.35 \) K. The dotted line (‘‘’’) shows the extrapolated real resistance, the white point (○), to \( Z_{Im} = 0 \).
Figure C.18. Comparison of experimental (•) and predicted (—) impedance data for a) NaOH in H$_2$O, and b) NaOD in D$_2$O at $T = 473.35$ K. The dotted line (‘‘’’) shows the extrapolated real resistance, the white point (○), to $Z_{\text{im}} = 0$. 
Figure C.19. Comparison of experimental (•) and predicted (—) impedance data for a) H$_2$O, and b) D$_2$O at $T = 498.17$ K. The dotted line (‘‘’) shows the extrapolated real resistance, the white point (○), to $Z_{\text{int}} = 0$. 
Figure C.20. Comparison of experimental (●) and predicted (—) impedance data for a) NaCl in H$_2$O, and b) NaCl in D$_2$O at $T = 498.17$ K. The dotted line (···) shows the extrapolated real resistance, the white point (⊙), to $Z_{Im} = 0$. 
Figure C.21. Comparison of experimental (●) and predicted (—) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 498.17$ K. The dotted line (···) shows the extrapolated real resistance, the white point (⊙), to $Z_{Im} = 0$.  

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Figure C.22. Comparison of experimental (●) and predicted (—) impedance data for a) NaCH₃COO in H₂O, and b) NaCH₃COO in D₂O at \( T = 498.17 \) K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to \( Z_{Im} = 0 \).
Figure C.23. Comparison of experimental (●) and predicted (—) impedance data for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 498.17$ K. The dotted line (‘‘·‘’) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.24. Comparison of experimental (●) and predicted (—) impedance data for a) NaOH in H₂O, and b) NaOD in D₂O at $T = 498.17$ K. The dotted line (···) shows the extrapolated real resistance, the white point (⊙), to $Z_{\text{im}} = 0$. 
Figure C.25. Comparison of experimental (●) and predicted (—) impedance data for a) H$_2$O, and b) D$_2$O at $T = 525.32$ K. The dotted line (‘•••’) shows the extrapolated real resistance, the white point (○), to $Z_{\text{Im}} = 0$. 
Figure C.26. Comparison of experimental (●) and predicted (—) impedance data for a) NaCl in H\(_2\)O, and b) NaCl in D\(_2\)O at \(T = 525.32\) K. The dotted line (‘.’) shows the extrapolated real resistance, the white point (∗), to \(Z_{\text{Im}} = 0\).
Figure C.27. Comparison of experimental (●) and predicted (–––) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 525.32$ K. The dotted line (‘···’) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.28. Comparison of experimental (●) and predicted (——) impedance data for a) NaCH$_3$COO in H$_2$O, and b) NaCH$_3$COO in D$_2$O at $T = 525.32$ K. The dotted line (‘…’) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.29. Comparison of experimental (●) and predicted (——) impedance data for a) HCl in H₂O, and b) DCl in D₂O at \( T = 525.32 \) K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to \( Z_{Im} = 0 \).
Figure C.30. Comparison of experimental (●) and predicted (—) impedance data for a) NaOH in H₂O, and b) NaOD in D₂O at \( T = 525.32 \) K. The dotted line (···) shows the extrapolated real resistance, the white point (⊙), to \( Z_{\text{Im}} = 0 \).
Figure C.31. Comparison of experimental (●) and predicted (—) impedance data for a) H$_2$O, and b) D$_2$O at $T = 548.44$ K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to $Z_{\text{Im}} = 0$. 
Figure C.32. Comparison of experimental (●) and predicted (—) impedance data for a) NaCl in H$_2$O, and b) NaCl in D$_2$O at \( T = 548.44 \) K. The dotted line (‘.’) shows the extrapolated real resistance the white point, (○), to \( Z_{Im} = 0 \).
Figure C.33. Comparison of experimental (●) and predicted (—) impedance data for a) CH$_3$COOH in H$_2$O, and b) CH$_3$COOD in D$_2$O at $T = 548.44$ K. The dotted line (‘·’) shows the extrapolated real resistance, the white point (⊙), to $Z_{Im} = 0$. 
Figure C.34. Comparison of experimental (○) and predicted (——) impedance data for a) NaCH$_3$COO in H$_2$O, and b) NaCH$_3$COO in D$_2$O at $T = 548.44$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 

![Diagram](image-url)
Figure C.35. Comparison of experimental (●) and predicted (—) impedance data for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 548.44$ K. The dotted line (···) shows the extrapolated real resistance, the white point (○), to $Z_{Im} = 0$. 
Figure C.36. Comparison of experimental (●) and predicted (——) impedance data for a) NaOH in H$_2$O, and b) NaOD in D$_2$O at $T = 548.44$ K. The dotted line (···) shows the extrapolated real resistance, the white point (⊙), to $Z_{\text{im}} = 0$. 
APPENDIX D

Calculation of Experimental Uncertainties
Uncertainties in values of $pK_{aq}$ for a weak acid in D$_2$O and H$_2$O were calculated using the standard propagation of error method (Harris, 2002). For measurements in the conductivity cell, diluted solutions (approximately $m = 10^{-3}$ mol·kg$^{-1}$) were prepared from the stock solutions using the appropriate solvent. The mass of the stock solution used in the dilution ($w_{\text{stock,dilute}}$) was weighed to a relative precision of ± 0.04 % and the mass of the solvent used to dilute the stock solution ($w_{\text{solvent,dilute}}$) was weighted to a relative precision of ± 0.01 %. For the diluted salt solutions, the absolute uncertainties in their molalities, $\delta m$, were based solely on the precision of the balances used (± 0.00002 g for our analytical balance and ± 0.02 g for our top-loading balance):

$$\frac{\delta m}{m} = \left(\frac{0.00002}{w_{\text{stock,dilute}}}\right)^2 + \left(\frac{0.02}{w_{\text{solvent,dilute}}}\right)^2 + \left(\frac{0.00002}{w_{\text{salt,stock}}}\right)^2 + \left(\frac{0.00002}{w_{\text{solvent,stock}}}\right)^2 \right)^{1/2} \quad (D.1)$$

$w_{\text{salt,stock}}$ was the mass of salt used to make the stock solution and $w_{\text{solvent,stock}}$ was the mass of solvent used to make the stock solution. For acids and bases prepared by standardization, equation (D.1) was modified in order to account for the uncertainty associated with standardizing the stock solutions, $\delta_{\text{standardization}}$. The resulting equation used was:

$$\frac{\delta m}{m} = \left(\frac{0.00002}{w_{\text{stock,dilute}}}\right)^2 + \left(\frac{0.02}{w_{\text{solvent,dilute}}}\right)^2 + \left(\frac{\delta_{\text{standardization}}}{m_{\text{stock}}}\right)^2 \right)^{1/2}, \quad (D.2)$$

where $m_{\text{stock}}$ was the molality of the stock solution, determined by standardization at 298.15 K. Using the standard propagation of uncertainty method reported by Skoog et al. (2007), the absolute uncertainty in the concentration was calculated from the absolute uncertainty of $m$: 

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\[ \delta c = \left( \frac{\delta m}{m} \right) \cdot c \]  

Uncertainties in \( \kappa_{\text{corr}} \) were calculated from the uncertainties in \( R_s, \delta R_s \) (which were obtained from the impedance extrapolation techniques described in Section 1.6.2), using the standard propagation of uncertainties method, also reported by Skoog et al. (2007):

\[ \delta \kappa_{\text{corr}} = \frac{k_{\text{cell}}}{(R_s)^2} \cdot \delta R_s \]  

Uncertainties in the experimental values of \( \Lambda^{\exp} \) for each system were calculated from uncertainties in \( \kappa_{\text{corr}}, \delta \kappa_{\text{corr}}, \) and \( c, \delta c, \) in a similar way:

\[ \delta \Lambda^{\exp} = \left( \left( \frac{1}{c} \right)^2 \cdot (\delta \kappa_{\text{corr}})^2 + \left( \frac{\kappa_{\text{corr}}}{c^2} \right)^2 \cdot (\delta c)^2 \right)^{1/2} \]  

Uncertainties in values of \( \Lambda^o \) were calculated for solutions of NaCl (H\(_2\)O), NaCl (D\(_2\)O), NaA (H\(_2\)O), NaA (D\(_2\)O), HCl, DCl, NaOH and NaOD from the uncertainties in values of \( \Lambda^{\exp} \):

\[ \delta \Lambda^o = ((\delta \Lambda^{\exp})^2 + (\delta c)^2)^{1/2}, \]  

and uncertainties in values of \( \Lambda^o \) values for HA and DA were calculated from the values of \( \delta \Lambda^o \) for the strong electrolytes, each of which were calculated using equation (D.6):

\[ \delta \Lambda_{HA}^o = ((\delta \Lambda_{HCl}^o)^2 + (\delta \Lambda_{NaCl}^o)^2 + (\delta \Lambda_{NaA}^o)^2)^{1/2} \]  

Uncertainties in values of \( K_a \) were calculated from uncertainties in \( m_{\text{aq}}, \Lambda^{\exp}, \) and \( \Lambda^o \) for HAc and DAc:

\[ \delta K_{\text{aq}} = K_{\text{aq}} \cdot \left( \frac{\delta \Lambda^{\exp}}{\Lambda^{\exp}} \right)^2 + \left( \frac{\delta \Lambda^o}{\Lambda^o} \right)^2 + \left( \frac{\delta m_{\text{aq}}}{m_{\text{aq}}} \right)^2 \right)^{1/2} \]
and uncertainties in $pK_{aq}$ for the weak acids were calculated using the standard propagation of uncertainties method for logarithms:

$$
\delta pK_{aq} = -\log(K_{aq}) - (-\log(\delta K_{aq} + K_{aq}))
$$  \hspace{1cm} (D.9)

Finally, uncertainties in $\Delta pK_{aq}$ were calculated from the uncertainties in $pK_{aq,H2O}$ and $pK_{aq,D2O}$:

$$
\delta(\Delta pK_{aq}) = (\delta pK_{aq,H2O})^2 + (\delta pK_{aq,D2O})^2)^{1/2}
$$  \hspace{1cm} (D.10)
APPENDIX E

Chapter 4
Table E.1.  Calculated Values for Parameters in Hnedkovsky extrapolation (Hnedkovsky et al., 2005) for KCl(aq), H$_3$PO$_4$(aq), KH$_2$PO$_4$(aq), HCl(aq), and KOH(aq) in H$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
<th>$b$</th>
<th>$d$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>55875.5 ± 445.0</td>
<td>0.00028 ± 0.00304</td>
<td>0.580 ± 0.063</td>
<td>55875.5 ± 445.0</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>343.4 ± 1.2</td>
<td>504.7 ± 137.7</td>
<td>0.602 ± 0.040</td>
<td>343.4 ± 1.2</td>
</tr>
<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>80.11 ± 0.18</td>
<td>143.3 ± 25.1</td>
<td>80.11 ± 0.18</td>
<td></td>
</tr>
<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>539.45 ± 0.57</td>
<td>941.5 ± 343.3</td>
<td>539.45 ± 0.57</td>
<td></td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>167.50 ± 0.11</td>
<td>174.7 ± 11.4</td>
<td>167.50 ± 0.11</td>
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</tr>
<tr>
<td>KOH(aq)</td>
<td>96.12 ± 0.28</td>
<td>144.9 ± 22.8</td>
<td>96.12 ± 0.28</td>
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</tbody>
</table>

$T = (298.174 ± 0.058)$ K, $p = (20.3024 ± 0.0031)$ MPa

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
<th>$b$</th>
<th>$d$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>33781.9 ± 3630.4</td>
<td>0.00014 ± 0.02365</td>
<td>0.627 ± 0.025</td>
<td>33781.9 ± 3630.4</td>
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<tr>
<td>KCl(aq)</td>
<td>1087.87 ± 0.37</td>
<td>541.1 ± 59.6</td>
<td>1087.87 ± 0.37</td>
<td></td>
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<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>111.211 ± 0.014</td>
<td>194.8 ± 4.1</td>
<td>111.211 ± 0.014</td>
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<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>1696.94 ± 0.57</td>
<td>630.7 ± 148.9</td>
<td>1696.94 ± 0.57</td>
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</tr>
<tr>
<td>HCl(aq)</td>
<td>740.81 ± 0.26</td>
<td>206.5 ± 22.7</td>
<td>740.81 ± 0.26</td>
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</tr>
<tr>
<td>KOH(aq)</td>
<td>416.84 ± 0.20</td>
<td>340.3 ± 68.0</td>
<td>416.84 ± 0.20</td>
<td></td>
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</table>

$T = (374.216 ± 0.075)$ K, $p = (21.2841 ± 0.0037)$ MPa
Table E.1.  Continued.

<table>
<thead>
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<th>System</th>
<th>$a$</th>
<th>$b$</th>
<th>$d$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = (423.295 \pm 0.048)$ K, $p = (21.3050 \pm 0.0055)$ MPa</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>H$_2$O</td>
<td>23436.9 ± 267.4</td>
<td>0.00114 ± 0.00174</td>
<td>23436.9 ± 267.4</td>
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<tr>
<td>KCl(aq)</td>
<td>784.58 ± 0.21</td>
<td>544.0 ± 56.2</td>
<td>0.692 ± 0.023</td>
<td>784.58 ± 0.21</td>
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<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>107.603 ± 0.012</td>
<td>235.8 ± 5.7</td>
<td>0.7701 ± 0.0053</td>
<td>107.603 ± 0.012</td>
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<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>1196.25 ± 0.33</td>
<td>555.4 ± 134.5</td>
<td>0.754 ± 0.054</td>
<td>1196.25 ± 0.33</td>
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<tr>
<td>HCl(aq)</td>
<td>618.79 ± 0.12</td>
<td>292.7 ± 32.9</td>
<td>0.697 ± 0.025</td>
<td>618.79 ± 0.12</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>345.39 ± 0.22</td>
<td>2632.1 ± 2283.6</td>
<td>1.32 ± 0.19</td>
<td>345.39 ± 0.22</td>
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</tbody>
</table>

<table>
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<tr>
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<th>$b$</th>
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<th>$R_s$</th>
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<tbody>
<tr>
<td>$T = (471.88 ± 0.10)$ K, $p = (21.2994 ± 0.0082)$ MPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18292.5 ± 148.4</td>
<td>0.00036 ± 0.00097</td>
<td>18292.5 ± 148.4</td>
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</tr>
<tr>
<td>KCl(aq)</td>
<td>209.120 ± 0.081</td>
<td>425.1 ± 40.6</td>
<td>0.782 ± 0.021</td>
<td>209.120 ± 0.081</td>
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<tr>
<td>H$_3$PO$_4$(aq)</td>
<td>54.175 ± 0.025</td>
<td>228.7 ± 12.7</td>
<td>0.783 ± 0.012</td>
<td>54.175 ± 0.025</td>
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<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>197.886 ± 0.055</td>
<td>401.3 ± 41.4</td>
<td>0.840 ± 0.023</td>
<td>197.886 ± 0.055</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>76.703 ± 0.010</td>
<td>244.2 ± 6.1</td>
<td>0.8067 ± 0.0055</td>
<td>76.703 ± 0.010</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>46.299 ± 0.033</td>
<td>132.4 ± 13.2</td>
<td>0.7500 ± 0.022</td>
<td>46.299 ± 0.033</td>
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Table E.1.  Continued.

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<td></td>
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<td>$\Omega$</td>
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<td>H$_2$O</td>
<td>17169.01 ± 127.9</td>
<td>-0.00007 ± 0.00087</td>
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<td>17169.01 ± 127.9</td>
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<td>KCl(aq)</td>
<td>124.649 ± 0.095</td>
<td>238.8 ± 15.9</td>
<td>0.627 ± 0.015</td>
<td>124.649 ± 0.095</td>
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<td>H$_3$PO$_4$(aq)</td>
<td>45.708 ± 0.080</td>
<td>74.9 ± 7.8</td>
<td>0.560 ± 0.024</td>
<td>45.708 ± 0.080</td>
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<tr>
<td>KH$_2$PO$_4$(aq)</td>
<td>196.77 ± 0.14</td>
<td>334.9 ± 46.5</td>
<td>0.715 ± 0.031</td>
<td>196.77 ± 0.14</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>82.55 ± 0.20</td>
<td>81.4 ± 14.3</td>
<td>0.525 ± 0.041</td>
<td>82.55 ± 0.20</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>52.445 ± 0.094</td>
<td>76.1 ± 6.5</td>
<td>0.519 ± 0.020</td>
<td>52.445 ± 0.094</td>
</tr>
</tbody>
</table>

$T = (498.02 ± 0.67)$ K, $p = (21.073 ± 0.011)$ MPa

$T = (523.56 ± 0.44)$ K, $p = (21.1355 ± 0.0042)$ MPa

H$_2$O  16865.4 ± 25.4  0.00002 ± 0.00017  16865.4 ± 25.4
KCl(aq) 119.75 ± 0.12  218.7 ± 17.7  0.614 ± 0.018  119.75 ± 0.12
H$_3$PO$_4$(aq) 56.848 ± 0.038  90.5 ± 5.5  0.611 ± 0.014  56.848 ± 0.038
KH$_2$PO$_4$(aq) 186.468 ± 0.055  333.8 ± 19.9  0.728 ± 0.013  186.468 ± 0.055
HCl(aq)  81.89 ± 0.16  60.5 ± 8.0  0.485 ± 0.032  81.89 ± 0.16
KOH(aq)  48.26 ± 0.089  68.0 ± 5.2  0.500 ± 0.018  48.26 ± 0.089
Table E.1. Continued.

<table>
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<tr>
<th>System</th>
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<th>( d )</th>
<th>( R_s )</th>
<th>( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>18030.6 ± 24.4</td>
<td>0.00005 ± 0.00017</td>
<td>0.689 ± 0.023</td>
<td>149.07 ± 0.11</td>
<td>38.873 ± 0.073</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>149.07 ± 0.11</td>
<td>275.2 ± 28.5</td>
<td>0.689 ± 0.023</td>
<td>18030.6 ± 24.4</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>H(_3)PO(_4)(aq)</td>
<td>78.300 ± 0.026</td>
<td>97.3 ± 4.9</td>
<td>0.644 ± 0.011</td>
<td>78.300 ± 0.026</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>KH(_2)PO(_4)(aq)</td>
<td>154.395 ± 0.080</td>
<td>211.3 ± 21.4</td>
<td>0.689 ± 0.023</td>
<td>154.395 ± 0.080</td>
<td>149.07 ± 0.11</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>93.667 ± 0.079</td>
<td>72.5 ± 6.8</td>
<td>0.545 ± 0.022</td>
<td>93.667 ± 0.079</td>
<td>38.873 ± 0.073</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>38.873 ± 0.073</td>
<td>75.6 ± 8.2</td>
<td>0.579 ± 0.025</td>
<td>38.873 ± 0.073</td>
<td>78.300 ± 0.026</td>
</tr>
</tbody>
</table>

\( T = (548.63 ± 0.20) \) K, \( p = (20.1351 ± 0.0058) \) MPa

<table>
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<th>( d )</th>
<th>( R_s )</th>
<th>( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>19902.2 ± 20.4</td>
<td>-0.00010 ± 0.00014</td>
<td>0.580 ± 0.025</td>
<td>18030.6 ± 24.4</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>148.72 ± 0.20</td>
<td>214.9 ± 22.8</td>
<td>0.580 ± 0.025</td>
<td>148.72 ± 0.20</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>H(_3)PO(_4)(aq)</td>
<td>103.092 ± 0.032</td>
<td>92.7 ± 4.1</td>
<td>0.591 ± 0.010</td>
<td>103.092 ± 0.032</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>KH(_2)PO(_4)(aq)</td>
<td>148.10 ± 0.11</td>
<td>159.5 ± 11.5</td>
<td>0.566 ± 0.017</td>
<td>148.10 ± 0.11</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>94.24 ± 0.11</td>
<td>56.9 ± 4.1</td>
<td>0.453 ± 0.018</td>
<td>94.24 ± 0.11</td>
<td>78.300 ± 0.026</td>
</tr>
<tr>
<td>KOH(aq)</td>
<td>55.327 ± 0.061</td>
<td>63.3 ± 3.5</td>
<td>0.500 ± 0.013</td>
<td>55.327 ± 0.061</td>
<td>78.300 ± 0.026</td>
</tr>
</tbody>
</table>

\( T = (571.91 ± 0.27) \) K, \( p = (21.1465 ± 0.0052) \) MPa
Table E.2. Calculated Values for Parameters in Hnedkovsky extrapolation (Hnedkovsky et al., 2005) for KCl(aq), D$_3$PO$_4$(aq), KD$_2$PO$_4$ (aq), DCl(aq), and KOD(aq) in D$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa.

<table>
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<tr>
<th>System</th>
<th>$a$</th>
<th>$b$</th>
<th>$d$</th>
<th>$R_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>41308.8 ± 39729.3</td>
<td>-0.01565 ± 0.27158</td>
<td>0.583 ± 0.063</td>
<td>41308.8 ± 39729.3</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>427.6 ± 1.5</td>
<td>643.3 ± 177.6</td>
<td>0.583 ± 0.063</td>
<td>427.6 ± 1.5</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>65.37 ± 0.17</td>
<td>110.0 ± 14.2</td>
<td>0.544 ± 0.030</td>
<td>65.37 ± 0.17</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>802.45 ± 0.37</td>
<td>1102.0 ± 206.0</td>
<td>0.789 ± 0.041</td>
<td>802.45 ± 0.37</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>59.31 ± 0.16</td>
<td>83.6 ± 7.6</td>
<td>0.481 ± 0.022</td>
<td>59.31 ± 0.16</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>305.2 ± 1.0</td>
<td>657.8 ± 427.3</td>
<td>0.75 ± 0.14</td>
<td>305.2 ± 1.0</td>
</tr>
</tbody>
</table>

$T = (298.174 ± 0.058)$ K, $p = (20.3024 ± 0.0031)$ MPa

<table>
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<th>$d$</th>
<th>$R_s$</th>
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<tbody>
<tr>
<td>D$_2$O</td>
<td>11021.9 ± 118.8</td>
<td>-0.00007 ± 0.00077</td>
<td>0.567 ± 0.013</td>
<td>11021.9 ± 118.8</td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>1284.29 ± 0.37</td>
<td>648.1 ± 37.6</td>
<td>0.567 ± 0.013</td>
<td>1284.29 ± 0.37</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>197.21 ± 0.16</td>
<td>156.8 ± 19.7</td>
<td>0.590 ± 0.029</td>
<td>197.21 ± 0.16</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>1834.58 ± 0.72</td>
<td>488.8 ± 61.1</td>
<td>0.546 ± 0.029</td>
<td>1834.58 ± 0.72</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>95.53 ± 0.15</td>
<td>112.2 ± 10.0</td>
<td>0.519 ± 0.021</td>
<td>95.53 ± 0.15</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>803.04 ± 0.48</td>
<td>670.6 ± 224.8</td>
<td>0.773 ± 0.074</td>
<td>803.04 ± 0.48</td>
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</table>

$T = (374.216 ± 0.075)$ K, $p = (21.2841 ± 0.0037)$ MPa
<table>
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<tbody>
<tr>
<td>D$_2$O</td>
<td>7098.6 ± 23.0</td>
<td>-0.00004 ± 0.00015</td>
<td>7098.6 ± 23.0</td>
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<tr>
<td>KCl(aq)</td>
<td>914.52 ± 0.33</td>
<td>540.5 ± 52.1</td>
<td>0.625 ± 0.022</td>
<td>914.52 ± 0.33</td>
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<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>191.519 ± 0.080</td>
<td>210.9 ± 20.6</td>
<td>0.689 ± 0.022</td>
<td>191.519 ± 0.080</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>1282.34 ± 0.65</td>
<td>400.5 ± 89.7</td>
<td>0.608 ± 0.051</td>
<td>1282.34 ± 0.65</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>77.838 ± 0.030</td>
<td>202.1 ± 11.0</td>
<td>0.740 ± 0.012</td>
<td>77.838 ± 0.030</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>721.87 ± 0.62</td>
<td>476.6 ± 138.2</td>
<td>0.670 ± 0.065</td>
<td>721.87 ± 0.62</td>
</tr>
</tbody>
</table>

$T = (423.295 \pm 0.048)$ K, $p = (21.3050 \pm 0.0055)$ MPa

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<td>D$_2$O</td>
<td>5115.3 ± 50.0</td>
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<td>5115.3 ± 50.0</td>
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<tr>
<td>KCl(aq)</td>
<td>129.31 ± 0.10</td>
<td>314.0 ± 25.1</td>
<td>0.680 ± 0.018</td>
<td>129.31 ± 0.10</td>
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<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>72.880 ± 0.032</td>
<td>225.3 ± 13.5</td>
<td>0.758 ± 0.013</td>
<td>72.880 ± 0.032</td>
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<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>193.04 ± 0.15</td>
<td>298.6 ± 42.1</td>
<td>0.700 ± 0.031</td>
<td>193.04 ± 0.15</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>24.4330 ± 0.0083</td>
<td>198.3 ± 4.2</td>
<td>0.7817 ± 0.0046</td>
<td>24.4330 ± 0.0083</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>107.881 ± 0.050</td>
<td>215.7 ± 29.0</td>
<td>0.805 ± 0.030</td>
<td>107.881 ± 0.050</td>
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</table>

$T = (471.88 ± 0.10)$ K, $p = (21.2994 ± 0.0082)$ MPa
Table E.2.  Continued.

<table>
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<tbody>
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<td>$D_2O$</td>
<td>21194.5 ± 462.9</td>
<td>0.00112 ± 0.00316</td>
<td>21194.5 ± 462.9</td>
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</tr>
<tr>
<td>KCl(aq)</td>
<td>160.25 ± 0.13</td>
<td>319.2 ± 24.2</td>
<td>0.645 ± 0.017</td>
<td>160.25 ± 0.13</td>
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</tr>
<tr>
<td>$D_3PO_4$(aq)</td>
<td>78.733 ± 0.026</td>
<td>109.0 ± 4.7</td>
<td>0.6394 ± 0.0097</td>
<td>78.733 ± 0.026</td>
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</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>216.70 ± 0.12</td>
<td>380.3 ± 41.0</td>
<td>0.726 ± 0.024</td>
<td>216.70 ± 0.12</td>
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<tr>
<td>DCI(aq)</td>
<td>30.22 ± 0.16</td>
<td>53.4 ± 9.1</td>
<td>0.498 ± 0.041</td>
<td>30.22 ± 0.16</td>
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</tr>
<tr>
<td>KOD(aq)</td>
<td>117.45 ± 0.17</td>
<td>102.6 ± 11.6</td>
<td>0.518 ± 0.027</td>
<td>117.45 ± 0.17</td>
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</tr>
</tbody>
</table>

$T = (498.02 \pm 0.67)$ K, $p = (21.073 \pm 0.011)$ MPa

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
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<th>$R_s$</th>
<th>$\Omega$</th>
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<tr>
<td>$D_2O$</td>
<td>21358.2 ± 500.2</td>
<td>0.00070 ± 0.00342</td>
<td>21358.2 ± 500.2</td>
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<tr>
<td>KCl(aq)</td>
<td>151.93 ± 0.13</td>
<td>262.9 ± 23.4</td>
<td>0.633 ± 0.020</td>
<td>151.93 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>$D_3PO_4$(aq)</td>
<td>97.855 ± 0.024</td>
<td>122.5 ± 6.0</td>
<td>0.678 ± 0.011</td>
<td>97.855 ± 0.024</td>
<td></td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>202.593 ± 0.053</td>
<td>353.5 ± 18.1</td>
<td>0.724 ± 0.011</td>
<td>202.593 ± 0.053</td>
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<tr>
<td>DCI(aq)</td>
<td>29.903 ± 0.077</td>
<td>28.3 ± 2.4</td>
<td>0.431 ± 0.021</td>
<td>29.903 ± 0.077</td>
<td></td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>104.83 ± 0.11</td>
<td>113.2 ± 9.4</td>
<td>0.544 ± 0.019</td>
<td>104.83 ± 0.11</td>
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$T = (523.56 \pm 0.44)$ K, $p = (21.1355 \pm 0.0042)$ MPa
Table E.2.  Continued.

<table>
<thead>
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<th>$R_s\Omega$</th>
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<td>D$_2$O</td>
<td>21942.3 ± 75.2</td>
<td>0.00083 ± 0.00051</td>
<td>21942.3 ± 75.2</td>
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</tr>
<tr>
<td>KCl(aq)</td>
<td>130.728 ± 0.079</td>
<td>292.1 ± 13.5</td>
<td>0.630 ± 0.010</td>
<td>130.728 ± 0.079</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>158.480 ± 0.029</td>
<td>127.4 ± 7.1</td>
<td>0.676 ± 0.012</td>
<td>158.480 ± 0.029</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>219.452 ± 0.068</td>
<td>464.7 ± 45.4</td>
<td>0.817 ± 0.021</td>
<td>219.452 ± 0.068</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>29.218 ± 0.049</td>
<td>33.4 ± 2.8</td>
<td>0.498 ± 0.020</td>
<td>29.218 ± 0.049</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>78.574 ± 0.085</td>
<td>95.5 ± 11.8</td>
<td>0.603 ± 0.028</td>
<td>78.574 ± 0.085</td>
</tr>
</tbody>
</table>

$T = (548.63 \pm 0.20) \text{ K}, \ p = (20.1351 \pm 0.0058) \text{ MPa}$

$T = (571.91 \pm 0.27) \text{ K}, \ p = (21.1465 \pm 0.0052) \text{ MPa}$

<table>
<thead>
<tr>
<th>System</th>
<th>$a$</th>
<th>$b$</th>
<th>$d$</th>
<th>$R_s\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>21420.2 ± 557.7</td>
<td>0.00234 ± 0.00381</td>
<td>21420.2 ± 557.7</td>
<td></td>
</tr>
<tr>
<td>KCl(aq)</td>
<td>127.30 ± 0.17</td>
<td>256.5 ± 20.8</td>
<td>0.591 ± 0.019</td>
<td>127.30 ± 0.17</td>
</tr>
<tr>
<td>D$_3$PO$_4$(aq)</td>
<td>207.965 ± 0.081</td>
<td>119.3 ± 11.4</td>
<td>0.605 ± 0.022</td>
<td>207.965 ± 0.081</td>
</tr>
<tr>
<td>KD$_2$PO$_4$(aq)</td>
<td>209.53 ± 0.26</td>
<td>234.4 ± 44.9</td>
<td>0.631 ± 0.043</td>
<td>209.53 ± 0.26</td>
</tr>
<tr>
<td>DCl(aq)</td>
<td>29.671 ± 0.064</td>
<td>23.7 ± 1.9</td>
<td>0.425 ± 0.020</td>
<td>29.671 ± 0.064</td>
</tr>
<tr>
<td>KOD(aq)</td>
<td>113.038 ± 0.045</td>
<td>123.2 ± 5.6</td>
<td>0.591 ± 0.010</td>
<td>113.038 ± 0.045</td>
</tr>
</tbody>
</table>
Table E.3. Values of $\rho$ and $\rho_{\text{H}_2\text{O}}$ for each solution in $\text{H}_2\text{O}$ at each of the temperature and pressure conditions reported in Chapter 4.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho_{\text{H}_2\text{O}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{KCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{H}_3\text{PO}_4}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{KH}_2\text{PO}_4}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{HCl}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{\text{KOH}}$ (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.174</td>
<td>20.3024</td>
<td>1.005964</td>
<td>1.006020</td>
<td>1.006130</td>
<td>1.006070</td>
<td>1.005980</td>
<td>1.006090</td>
</tr>
<tr>
<td>374.216</td>
<td>21.2841</td>
<td>0.967266</td>
<td>0.967273</td>
<td>0.967331</td>
<td>0.967278</td>
<td>0.967268</td>
<td>0.967279</td>
</tr>
<tr>
<td>423.295</td>
<td>21.3050</td>
<td>0.928247</td>
<td>0.928255</td>
<td>0.928311</td>
<td>0.928259</td>
<td>0.928249</td>
<td>0.928260</td>
</tr>
<tr>
<td>471.88</td>
<td>21.2994</td>
<td>0.880236</td>
<td>0.880263</td>
<td>0.880432</td>
<td>0.880302</td>
<td>0.880259</td>
<td>0.880329</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
<td>0.849848</td>
<td>0.849891</td>
<td>0.850160</td>
<td>0.849908</td>
<td>0.849872</td>
<td>0.849927</td>
</tr>
<tr>
<td>523.56</td>
<td>21.1355</td>
<td>0.816638</td>
<td>0.816685</td>
<td>0.816938</td>
<td>0.816701</td>
<td>0.816666</td>
<td>0.816730</td>
</tr>
<tr>
<td>548.63</td>
<td>20.1351</td>
<td>0.778106</td>
<td>0.778148</td>
<td>0.778374</td>
<td>0.778185</td>
<td>0.778137</td>
<td>0.778241</td>
</tr>
<tr>
<td>571.91</td>
<td>21.1465</td>
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<td>0.739091</td>
<td>0.739290</td>
<td>0.739128</td>
<td>0.739081</td>
<td>0.739151</td>
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Table E.4. Values of $\rho$ and $\rho_{D_{2}O}$ for each solution in $D_{2}O$ at each of the temperature and pressure conditions reported in Chapter 4.

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<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho_{D_{2}O}$ (g·cm$^{-3}$)</th>
<th>$\rho_{KCl}$ (g·cm$^{-3}$)</th>
<th>$\rho_{D_{3}PO_{4}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{KD_{2}PO_{4}}$ (g·cm$^{-3}$)</th>
<th>$\rho_{DCl}$ (g·cm$^{-3}$)</th>
<th>$\rho_{KOD}$ (g·cm$^{-3}$)</th>
</tr>
</thead>
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<td>20.3024</td>
<td>1.114708</td>
<td>1.114760</td>
<td>1.115110</td>
<td>1.114790</td>
<td>1.114770</td>
<td>1.114770</td>
</tr>
<tr>
<td>374.216</td>
<td>21.2841</td>
<td>1.073327</td>
<td>1.073330</td>
<td>1.073380</td>
<td>1.073340</td>
<td>1.073350</td>
<td>1.073340</td>
</tr>
<tr>
<td>423.295</td>
<td>21.3050</td>
<td>1.029889</td>
<td>1.029900</td>
<td>1.029940</td>
<td>1.029900</td>
<td>1.029910</td>
<td>1.029900</td>
</tr>
<tr>
<td>471.88</td>
<td>21.2994</td>
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<td>0.975863</td>
<td>0.976075</td>
<td>0.975888</td>
<td>0.975909</td>
<td>0.975867</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
<td>0.941453</td>
<td>0.941492</td>
<td>0.941749</td>
<td>0.941514</td>
<td>0.941536</td>
<td>0.941498</td>
</tr>
<tr>
<td>523.56</td>
<td>21.1355</td>
<td>0.903896</td>
<td>0.903939</td>
<td>0.904181</td>
<td>0.903960</td>
<td>0.903995</td>
<td>0.903950</td>
</tr>
<tr>
<td>548.63</td>
<td>20.1351</td>
<td>0.860272</td>
<td>0.860328</td>
<td>0.860460</td>
<td>0.860333</td>
<td>0.860402</td>
<td>0.860355</td>
</tr>
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<td>0.815933</td>
<td>0.816041</td>
<td>0.815935</td>
<td>0.816032</td>
<td>0.815934</td>
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</tbody>
</table>
Table E.5. Values of $V^\circ$ for $\ce{K+}$, $\ce{Cl-}$, $\ce{H3PO4}$, $\ce{H2PO4-}$ and $\ce{OH-}$ in $\ce{H2O}$ at each of the temperature and pressure conditions reported in Chapter 4, obtained from SUPCRT (Johnson et al. 1992).

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p$</th>
<th>$V_{\ce{K+}}^\circ$</th>
<th>$V_{\ce{Cl-}}^\circ$</th>
<th>$V_{\ce{H3PO4}}^\circ$</th>
<th>$V_{\ce{H2PO4-}}^\circ$</th>
<th>$V_{\ce{OH-}}^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>47.2</td>
<td>30.7</td>
<td>-3.9</td>
</tr>
<tr>
<td>374.216</td>
<td>21.2841</td>
<td>10.7</td>
<td>16.3</td>
<td>50.9</td>
<td>31.0</td>
<td>-4.5</td>
</tr>
<tr>
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<td>21.3050</td>
<td>10.4</td>
<td>12.7</td>
<td>52.3</td>
<td>28.1</td>
<td>-8.6</td>
</tr>
<tr>
<td>471.88</td>
<td>21.2994</td>
<td>9.7</td>
<td>5.6</td>
<td>54.0</td>
<td>21.9</td>
<td>-16.7</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
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<td>-1.1</td>
<td>55.3</td>
<td>15.9</td>
<td>-24.3</td>
</tr>
<tr>
<td>523.56</td>
<td>21.1355</td>
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<td>-11.5</td>
<td>57.3</td>
<td>6.5</td>
<td>-36.2</td>
</tr>
<tr>
<td>548.63</td>
<td>20.1351</td>
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<td>-29.6</td>
<td>60.7</td>
<td>-10.1</td>
<td>-56.6</td>
</tr>
<tr>
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<td>21.1465</td>
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<td>-57.2</td>
<td>66.0</td>
<td>-35.6</td>
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</table>
Table E.6. Values of $\rho$, $\eta$ and $\varepsilon$ for H$_2$O and D$_2$O at each of the temperature and pressure conditions reported in Chapter 4.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$p$ (MPa)</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>$\eta$</th>
<th>$\varepsilon$</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>$\eta$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.174</td>
<td>20.3024</td>
<td>1.005964</td>
<td>0.008859</td>
<td>79.14</td>
<td>1.114708</td>
<td>0.010880</td>
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</tr>
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<td>0.976266</td>
<td>0.002843</td>
<td>55.98</td>
<td>1.073327</td>
<td>0.003326</td>
<td>55.75</td>
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<td>0.001875</td>
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<td>1.029889</td>
<td>0.002166</td>
<td>44.56</td>
</tr>
<tr>
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<td>0.001400</td>
<td>35.78</td>
<td>0.975815</td>
<td>0.001590</td>
<td>35.63</td>
</tr>
<tr>
<td>498.02</td>
<td>21.073</td>
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<td>0.001234</td>
<td>31.60</td>
<td>0.941453</td>
<td>0.001387</td>
<td>31.40</td>
</tr>
<tr>
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<td>0.903896</td>
<td>0.001231</td>
<td>27.75</td>
</tr>
<tr>
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<td>20.1351</td>
<td>0.778106</td>
<td>0.000995</td>
<td>24.37</td>
<td>0.860272</td>
<td>0.001099</td>
<td>24.27</td>
</tr>
<tr>
<td>571.91</td>
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<td>0.000909</td>
<td>21.36</td>
<td>0.815867</td>
<td>0.000997</td>
<td>21.25</td>
</tr>
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</table>
Table E.7. Values of $pK_w$, $pK_1$, and $pK_2$, for equilibrium reactions (4.10) and (4.11), corresponding degrees of hydrolysis, $\alpha_2$, ionization, $\beta_2$, and amphiprotic ionization $\beta_2 + \alpha_2$, experimental aquamolalities, $m_{aq}$, equilibrium aquamolalities, $m_{aq,eq}$, molar conductivities, $\Lambda^{\exp}$, equilibrium molar conductivities, $\Lambda^{\exp,eq}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for $\text{KH}_2\text{PO}_4$(aq) in H$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>$T^*$ K</th>
<th>$p^*$ MPa</th>
<th>$pK_w$</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
<th>$\beta_2$</th>
<th>$\alpha_2$</th>
<th>$\beta_2 + \alpha_2$</th>
<th>$m_{aq} \cdot 10^6*$</th>
<th>$m_{aq,eq} \cdot 10^6*$</th>
<th>$\Lambda^{\exp}$</th>
<th>$\Lambda^{\exp,eq}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.174</td>
<td>20.3024</td>
<td>13.915</td>
<td>2.110</td>
<td>7.114</td>
<td>0.0087</td>
<td>0.0011</td>
<td>0.0099</td>
<td>1154.53</td>
<td>1143.13</td>
<td>102.44</td>
<td>102.34</td>
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<td>0.0010</td>
<td>0.0223</td>
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<td>129.80</td>
<td>297.68</td>
<td>295.75</td>
<td>298.88</td>
</tr>
<tr>
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<td>11.555</td>
<td>2.853</td>
<td>7.431</td>
<td>0.0140</td>
<td>0.0019</td>
<td>0.0159</td>
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<td>443.71</td>
<td>448.74</td>
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<tr>
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<td>0.0046</td>
<td>0.0106</td>
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<td>551.94</td>
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<td>11.104</td>
<td>3.393</td>
<td>7.963</td>
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<td>0.0059</td>
<td>0.0105</td>
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<td>635.17</td>
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<td>0.0077</td>
<td>0.0110</td>
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<td>608.95</td>
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<td>697.31</td>
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<td>0.0119</td>
<td>728.59</td>
<td>719.90</td>
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<td>747.06</td>
<td>778.35</td>
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<td>718.80</td>
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<td>819.26</td>
<td>853.92</td>
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</table>

*Uncertainties in the temperature and pressure are reported in Table 4.1*
Table E.8. Values of $pK_w$, $pK_1$, and $pK_2$, for equilibrium reactions (4.10) and (4.11), corresponding degrees of hydrolysis, $\alpha_2$, ionization, $\beta_2$, and amphiprotic ionization $\beta_2 + \alpha_2$, experimental aquamolalities, $m_{aq}$, equilibrium aquamolalities, $m_{aq,eq}$, molar conductivities, $\Lambda^{exp}$, equilibrium molar conductivities, $\Lambda^{exp,eq}$, and fitted limiting molar conductivities, $\Lambda^\circ$ for KD$_2$PO$_4$(aq) in D$_2$O from $T = 298$ K to $T = 571$ K at $p = 20$ MPa.

<table>
<thead>
<tr>
<th>$T^\ast$ (K)</th>
<th>$p^\ast$ (MPa)</th>
<th>$pK_w$</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
<th>$\beta_2$</th>
<th>$\alpha_2$</th>
<th>$\beta_2 + \alpha_2$</th>
<th>KD$_2$PO$_4$(aq)</th>
<th>$m_{aq,10^6}$</th>
<th>$m_{aq,eq,10^6}$</th>
<th>$\Lambda^{exp}$</th>
<th>$\Lambda^{exp,eq}$</th>
<th>$\Lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>20.3024</td>
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<td>2.110</td>
<td>7.114</td>
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<td>0.0010</td>
<td>0.0111</td>
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<tr>
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<td>0.0165</td>
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<td>118.97</td>
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<tr>
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<td>21.2994</td>
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<td>3.192</td>
<td>7.752</td>
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<td>0.0046</td>
<td>0.0106</td>
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</tr>
<tr>
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<td>11.104</td>
<td>3.393</td>
<td>7.963</td>
<td>0.0045</td>
<td>0.0060</td>
<td>0.0105</td>
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<td>11.151</td>
<td>4.106</td>
<td>8.757</td>
<td>0.0017</td>
<td>0.0132</td>
<td>0.0149</td>
<td>557.75</td>
<td>549.44</td>
<td>772.90</td>
<td>774.3</td>
<td>803.6</td>
<td></td>
</tr>
</tbody>
</table>

*Uncertainties in the temperature and pressure are reported in Table 4.2.
Figure E.1. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $f^b$ for a) H$_2$O, and b) D$_2$O at $T = 298.174$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $f = 0$. 
Figure E.2. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^2w)$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 298.174$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.3. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f)^{a_w}$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 298.174$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.4. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha_w})$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 298.174$ K. The dotted line (‘····’) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.5. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha W})$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 298.174$ K. The dotted line (······) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
**Figure E.6.** Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/ f^{α_w})$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 298.174$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.7. Comparison of experimental (●) and predicted (---) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 374.216$ K. The dotted line (····) shows the extrapolated real resistance, the white point, (○), to $f = 0$. 
Figure E.8. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^\alpha_w)$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 374.216$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.9. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha_w})$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 374.216$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 


Figure E.10. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^a_w)$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 374.216$ K. The dotted line (····) shows the extrapolated real resistance, the white point, (⊙), to $f = \infty$. 
Figure E.11. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{α_w})$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 374.216$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = ∞$. 
Figure E.12. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/\phi W)$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 374.216$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.13. Comparison of experimental (•) and predicted (—) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 423.295$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = 0$. 
Figure E.14. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\infty})$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 423.295$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.15. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha W})$ for a) $\text{H}_3\text{PO}_4$ in $\text{H}_2\text{O}$, and b) $\text{D}_3\text{PO}_4$ in $\text{D}_2\text{O}$ at $T = 423.295$ K. The dotted line (····) shows the extrapolated real resistance, the white point, (○), to $f = \infty$. 
Figure E.16. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha})$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 423.295$ K. The dotted line (⋯⋯) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
**Figure E.17.** Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha_w})$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 423.295$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.18. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^\alpha W)$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 423.295$ K. The dotted line (· · · · ) shows the extrapolated real resistance, the white point, (○), to $f = \infty$. 
Figure E.19. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 471.88$ K. The dotted line (· · · ··) shows the extrapolated real resistance, the white point (○), to $f = 0$. 
Figure E.20. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^{ow})$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 471.88$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.21. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{α_w})$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 471.88$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.22. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^\omega)$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 471.88$ K. The dotted line (-----) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.23. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\infty \omega})$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 471.88$ K. The dotted line (•••) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.24. Comparison of experimental (●) and predicted (―) values of $Z_{Re}$ vs. $(1/f^\alpha_w)$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 471.88$ K. The dotted line (‘‘‘‘) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.25. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 498.02$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = 0$. 

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Figure E.26. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{sw})$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 498.02$ K. The dotted line (·····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.27. Comparison of experimental (●) and predicted (---) values of $Z_{Re}$ vs. $(1/f^aW)$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 498.02$ K. The dotted line (· · · ·) shows the extrapolated real resistance, the white point (◇), to $f = \infty$. 
Figure E.28. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{\alpha})$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 498.02$ K. The dotted line (••••) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.29. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^a)$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 498.02$ K. The dotted line (·····) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.30. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{cw})$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 498.02$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.31. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $f^2$ for a) $\text{H}_2\text{O}$, and b) $\text{D}_2\text{O}$ at $T = 523.56$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = 0$. 
Figure E.32. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^\alpha)$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 523.56$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.33. Comparison of experimental (●) and predicted (—— ) values of $Z_{Re}$ vs. $(1/f^{\alpha \omega} )$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 523.56$ K. The dotted line (····) shows the extrapolated real resistance, the white point, (○), to $f = \infty$. 
Figure E.34. Comparison of experimental (●) and predicted (——) values of $Z_{\text{Re}}$ vs. $(1 / f^{\alpha \omega})$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 523.56$ K. The dotted line (· · · ·) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.35. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f_{\alpha w}^*)$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 523.56$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.36. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^{aw})$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 523.56$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.37. Comparison of experimental (■) and predicted (—) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 548.63$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $f = 0$. 
Figure E.38. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{aw})$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 548.63$ K. The dotted line (...) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.39. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f_{\omega}^{aw})$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 548.63$ K. The dotted line (・・・) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.40. Comparison of experimental (●) and predicted ( — ) values of $Z_{Re}$ vs. $(1/f^\alpha)$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 548.63$ K. The dotted line (· · · ·) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 

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Figure E.41. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^{αW})$ for a) HCl in H$_2$O, and b) DCl in D$_2$O at $T = 548.63$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
**Figure E.42.** Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f)^{aw}$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 548.63$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$.  

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Figure E.43. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $f^2$ for a) H$_2$O, and b) D$_2$O at $T = 571.91$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = 0$. 
Figure E.44. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1 / f^{a_w})$ for a) KCl in H$_2$O, and b) KCl in D$_2$O at $T = 571.91$ K. The dotted line (····) shows the extrapolated real resistance, the white point (○), to $f = \infty$. 
Figure E.45. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{a_w})$ for a) H$_3$PO$_4$ in H$_2$O, and b) D$_3$PO$_4$ in D$_2$O at $T = 571.91$ K. The dotted line (· · · ·) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.46. Comparison of experimental (●) and predicted (——) values of $Z_{Re}$ vs. $(1/f^{*\alpha})$ for a) KH$_2$PO$_4$ in H$_2$O, and b) KD$_2$PO$_4$ in D$_2$O at $T = 571.91$ K. The dotted line (····) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 
Figure E.47. Comparison of experimental (●) and predicted (—) values of $Z_{Re}$ vs. $(1/f^{aw})$ for a) HCl in H₂O, and b) DCl in D₂O at $T = 571.91$ K. The dotted line (· · ·) shows the extrapolated real resistance, the white point (○), to $f = ∞$. 
Figure E.48. Comparison of experimental (○) and predicted (---) values of $Z_{Re}$ vs. $(1/f^{aw})$ for a) KOH in H$_2$O, and b) KOD in D$_2$O at $T = 571.91$ K. The dotted line (· · · ·) shows the extrapolated real resistance, the white point (⊙), to $f = \infty$. 