Structural Characteristics and Thermophysical Properties of Molten Salts From Ab Initio Molecular Dynamics Simulations

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Structural Characteristics and Thermophysical Properties
of Molten Salts from Ab Initio Molecular
Dynamics Simulations

Austin David Clark

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

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ABSTRACT

Structural Characteristics and Thermophysical Properties of Molten Salts from Ab Initio Molecular Dynamics Simulations

Austin David Clark
Department of Chemical Engineering, BYU
Doctor of Philosophy

This work 1) draws insights on molten salt structure and properties directly from ab initio molecular dynamics (AIMD) simulations, 2) demonstrates the advantageous symbiosis of computational and experimental collaborations on molten salt research, and 3) simultaneously generates ab initio data sets for fitting an interatomic potential model for classical molecular dynamics (MD) simulations.

This work discusses the motivations for AIMD simulations of molten salts, thermophysical properties and structural characteristics of interest, advanced methodologies for AIMD simulations, and several completed AIMD studies on molten salts.

Of import are the methodological contributions of this work to AIMD simulations, primarily the radical increase in generalized gradient planewave energy cutoff used to more accurately model the electron distribution across a highly-polarizable molten salt. Cutoffs of up to 2500 Rydbergs are used in this work, but 2000 Rydbergs is found to be sufficient for most AIMD NpT modelling of molten fluorides\(^1,2\).

The equilibrium liquid density of eutectic FLiNaK as a function of temperature is found to agree with the experimental density reported by Chrenkova et al.\(^3\) to within 0.2%, and the equilibrium liquid density of eutectic FMgNaK is found to agree with experimental measurements reported herein to within 4%. Self-diffusion coefficients in FMgNaK are also considered, with applicability to other halide salts.

Molybdenum, Cesium, iodide, nickel, hydrogen, oxide, and uranium complexation are examined. It is found that solvation strength can be qualitatively determine via AIMD simulations, and that poorly solvated solutes will minimize the surface area of interaction with the salt solution. Cesium in particular is shown to be volatile or retainable in FLiBe at 500, 650, and 800 °C based on complexation and validated experimentally.

It is shown that the chemical potential of an anion varies between melts as influenced by the different cations present in each melt. Hence, attempts to use a common electrochemical reference reaction for different salt mixtures are at best an approximation\(^4\).

Keywords: molten salt, AIMD, FLiNaK, FLiBe, KLiCl, FMgNaK, solutes, QTAIM, CP2K
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# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ ii

TABLE OF CONTENTS ................................................................................................................ iv

LIST OF TABLES .......................................................................................................................... x

LIST OF FIGURES ....................................................................................................................... xii

1 Introduction ................................................................................................................................... 1

2 Motivations to Understand Molten Salt Solvation Characteristics ........................................ 4

2.1 The First Motivation: Targeted Alpha Therapy ................................................................. 4

2.1.1 Targeted Alpha Therapy Background ........................................................................... 4

2.1.2 Bismuth-213 Generation ............................................................................................... 5

2.2 The Second Motivation: Improved Nuclear Energy ........................................................ 6

2.2.1 An Overview of Nuclear Energy in the United States of America ............................... 6

2.2.2 The Molten Salt Nuclear Reactor ................................................................................. 8

2.3 The Third Motivation: Molten Salts in Thermodynamic Cycles .................................... 10

2.4 Additional Motivations: Molybdenum-99 and Other Rare Isotopes ............................. 11

2.4.1 One Man’s Trash: The Market for Fission Products ................................................... 11

2.4.2 Continuous Separation ................................................................................................. 12

2.4.3 Economic Feasibility .................................................................................................... 13

2.5 The Common Challenges .................................................................................................... 15
3 Motivations to Study Molten Salt Chemistry Using Ab Initio Molecular Dynamics. .............................................................................................................. 18

3.1 The Experimental Predicament .............................................................................................................. 18

3.2 Molecular Dynamics Simulations .......................................................................................................... 19

3.3 Ab Initio Molecular Dynamics Simulations .......................................................................................... 22

4 Thermophysical Properties and Structural Characteristics .................................................................................. 24

4.1 Properties and Characteristics to be Predicted from AIMD .................................................................. 24

4.1.1 Salt Structure .................................................................................................................................. 24

4.1.2 Density ........................................................................................................................................... 25

4.1.3 Diffusion Coefficients ................................................................................................................... 25

4.1.4 Bader Charge .................................................................................................................................. 26

4.2 Properties that May be Predicted from Classical MD ........................................................................... 27

4.2.1 Viscosity ......................................................................................................................................... 27

4.2.2 Thermal Conductivity .................................................................................................................. 28

4.2.3 Heat Capacity .................................................................................................................................. 29

5 Requirements ............................................................................................................................................. 30

5.1 Salts of Interest ....................................................................................................................................... 31

5.2 Solutes of Interest ................................................................................................................................. 32

5.3 Additional Interests ............................................................................................................................... 32

6 Methodology of Ab Initio Molecular Dynamics of Molten Salts ..................................................................... 33

6.1 An Introduction to Molecular Dynamics ............................................................................................... 33
6.2 Ab Initio Molecular Dynamics................................................................. 34

6.2.1 Density Functional Theory ............................................................... 35

6.3 CP2K: An Ab Initio Molecular Dynamics Software Package ............. 38

6.4 Additional Computational Tools and Software ....................................... 41

6.4.1 PACKMOL......................................................................................... 41

6.4.2 VMD................................................................................................. 41

6.4.3 The Henkleman Group Bader Code ................................................... 42

6.4.4 The Fulton Supercomputing Lab........................................................ 42

7 Pure Molten FLiNaK: Its Density and Structure ....................................... 43

8 Characterization of the Molten Salt FMgNaK through Experimentally-Validated
Ab Initio Molecular Dynamics................................................................. 56

8.1 Introduction to the Characterization of the Molten Salt FMgNaK .......... 56

8.2 Methodology for the Characterization of FMgNaK ................................ 59

8.2.1 Simulation Methods........................................................................... 59

8.2.2 Experimental Methods...................................................................... 63

8.3 Characterization Results of the Molten Salt FMgNaK and Discussion .... 68

8.3.1 Note on Simulation Equilibration....................................................... 68

8.3.2 Density............................................................................................. 68

8.3.3 Coefficient of Thermal Expansion .................................................... 70

8.3.4 Structural Information ...................................................................... 71
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 On the Electrochemical Thermodynamics of Minor Components in Molten Salt Mixtures.</td>
<td>119</td>
</tr>
<tr>
<td>10.1 Introduction to the Electrochemical Thermodynamics of Minor Components in Molten Salt Mixtures</td>
<td>119</td>
</tr>
<tr>
<td>10.2 The Importance of the Standard State in Defining Activity Coefficients</td>
<td>121</td>
</tr>
<tr>
<td>10.3 The Standard State from Infinite Dilution for Minor Components</td>
<td>126</td>
</tr>
<tr>
<td>10.4 Comparison of Infinite Dilution and Pure Component Standard States</td>
<td>130</td>
</tr>
<tr>
<td>10.5 Implications of Infinite Dilution Standard States for the Activity of Cations</td>
<td>133</td>
</tr>
<tr>
<td>10.6 Salt-Specific Effects</td>
<td>135</td>
</tr>
<tr>
<td>10.7 Data Supporting the Variation in Activity between Different Salt Melts</td>
<td>138</td>
</tr>
<tr>
<td>10.7.1 Experimental Data</td>
<td>138</td>
</tr>
<tr>
<td>10.7.2 Ab initio molecular dynamics (AIMD) simulations</td>
<td>140</td>
</tr>
<tr>
<td>10.8 Redox Potential Series Based on the Infinite Dilution Standard State</td>
<td>144</td>
</tr>
<tr>
<td>10.9 Multiple-Anion Effects</td>
<td>147</td>
</tr>
<tr>
<td>10.10 Published Conclusions</td>
<td>151</td>
</tr>
<tr>
<td>11 Cesium Fluoride Retention and Volatility in Molten FLiBe</td>
<td>153</td>
</tr>
<tr>
<td>11.1 Introduction to Cesium Fluoride Retention and Volatility in Molten FLiBe</td>
<td>153</td>
</tr>
<tr>
<td>11.2 Methodology for Examining CsF Retention and Volatility in Molten FLiBe</td>
<td>154</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Experimental Concentration Measurement</td>
</tr>
<tr>
<td>11.2.2</td>
<td>AIMD Simulation Details</td>
</tr>
<tr>
<td>11.3</td>
<td>CsF Retention Study Results and Discussion</td>
</tr>
<tr>
<td>11.3.1</td>
<td>Experimental Results</td>
</tr>
<tr>
<td>11.3.2</td>
<td>AIMD Results</td>
</tr>
<tr>
<td>11.3.3</td>
<td>Additional Discussion</td>
</tr>
<tr>
<td>11.4</td>
<td>Conclusions on CsF Retention and Volatility in Molten FLiBe</td>
</tr>
<tr>
<td>12</td>
<td>Water, Nickel, and Nickel Oxide Behavior in Molten FLiNaK</td>
</tr>
<tr>
<td>12.1</td>
<td>Introduction to Water, Nickel, and Nickel Oxide Behavior in Molten FLiNaK</td>
</tr>
<tr>
<td>12.2</td>
<td>Study on Water, Nickel, and Nickel Oxide Behavior in Molten FLiNaK</td>
</tr>
<tr>
<td>12.3</td>
<td>Conclusions from the Study on Water, Nickel and Nickel Oxide Behavior in Molten FLiNaK</td>
</tr>
<tr>
<td>13</td>
<td>Ongoing Projects and Future Work</td>
</tr>
<tr>
<td>14</td>
<td>Conclusions</td>
</tr>
<tr>
<td></td>
<td>References</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 7-1. Nearest-neighbor (NN) peak distances and coordination numbers for various ion pairs determined from the AIMD simulations and an earlier x-ray scattering study. 55

Table 8-1. A list of the simulated temperatures and the number of simulations conducted at each temperature. 61

Table 8-2: Coefficients of the linear density models. The additive model was calculated from a weighted average of molar volumes for KF, MgF2, and NaF from Cantor et al. 70

Table 8-3: Comparison between the first-peak radius and coordination number found in our AIMD simulations at 800 °C with those found experimentally in similar salts. 73

Table 8-4: Equilibrated simulations that contained chaining events. 76

Table 8-5: Results from Bader analysis averaged across our 19 equilibrated simulations. Error bounds represent a 95% confidence interval. 79

Table 9-1. Complexes formed by 3 Mo atoms in FLiNaK at 950K, by formal oxidation state of Mo. 91

Table 9-2. Fluoride coordination number for each mononuclear Mo species identified in simulations at 950 K. The fluoride number density weighted integrals of the RDFs shown in Figure 9-3 were evaluated from 0 to 2.8 Å. 96

Table 9-3. Bader charges of Mo complexes observed at 950K. 98

Table 10-1. Measured data from Hamby for potential of CoCl2 at 1073 K. 131

Table 10-2. Comparison of various reactions’ standard potentials compiled by Plambeck, standard potentials referenced to the molality scale. Many reactions’ standard potentials.
are extremely similar between the two melts but some are not; those that are not are marked in red and italicized ................................................................. 137

Table 10-3. Intercept Potentials (E_{int} from Equation 10-15) from infinite dilution extrapolation for NiCl$_2$ and CoCl$_2$ in various solvents at 1073 K ............................................. 140

Table 10-4. Regressed standard potentials for various lanthanides and americium vs Ag/AgCl in LiCl-KCl eutectic. Data used in linear regression taken from Fusselman et al$^{247}$ ................................................................................................................. 145

Table 10-5. Parameters for linear regressions of standard potential vs temperature for data from Table 10-4 .................................................................................................................................................. 145

Table 10-6. Cesium coordination with fluoride ions at various concentrations of CsF and CsI as calculated by AIMD simulations ......................................................................................................................... 148
Figure 6-1. AIMD simulation of a FLiNaK system containing MoF$_3$ and UF$_4$. The system is mirrored using periodic boundary conditions for illustration purposes. Here yellow is U, light blue is Mo, green is F, purple is Li, dark blue is Na, and pink is K. A brief movie of this or other salt systems illustrated in this work in motion can be obtained by contacting the author. These movies will also bring new meaning to the phrase ordo ab chao. .................................................................................................................................. 37

Figure 6-2. The density of a FLiNaK cell at 940K over time as the energy cutoffs were gradually increased. The final cutoff and relative cutoff values were 2000 Ry and 120 Ry respectively. .............................................................................................................. 40

Figure 7-1. Density of FLiNaK determined from the AIMD simulations in the present work (blue circles, with the solid turquoise line showing a linear fit) compared to experimentally estimated values from An et al, Chrenkova et al., and Powers et al.$^3, 140, 141$ .................................................................................................................. 47

Figure 7-2. Total scattering structure function S(Q) for molten FLiNaK at 467 °C and 980 °C, offset vertically for clarity. .............................................................................................................. 49

Figure 7-3. The PDF g(r) of FLiNaK at various temperatures below and above the melting point. The solid-liquid transition is clearly seen through the loss of well-defined features at high r above the melting point. .................................................................................................................. 51

Figure 7-4. (a) Observed PDF and calculated PDF determined from AIMD simulations of FLiNaK. The excellent agreement demonstrates that the simulations provide an accurate picture of the structure of molten FLiNaK. (b) The partial PDFs g$_{\alpha\beta}$ extracted
from the AIMD simulations, displayed over the first 5 Å. Note that these partial PDFs have not been weighted by the concentrations or scattering lengths of the ions.

Figure 8-1: BYU Molten Salt Laboratory Archimedean method density apparatus diagram. a – Mettler Toledo analytical scale with hook for mass underneath: model ML503T or MS303TS, b – stainless steel heavy duty scissor lift, c – Paragon SC-2 Pro Furnace with Orton SntryXpress 5.0 Controller, d – Omega Industry Type-K thermocouple, e – nickel wire, f – nickel bob.

Figure 8-2: Density measurements of FMgNaK as a function of temperature. Green lines represent a 95% confidence band on the model.

Figure 8-3: Snapshot of AIMD trajectory for FMgNaK at 1073 °C. Colors green, orange, blue, and purple correspond to elements F, Mg, Na, and K, respectively.

Figure 8-4: Radial distribution functions (RDF) of FMgNaK at 800 °C. This analysis was performed on each simulation to check for temperature dependence, and variance across temperatures was minimal.

Figure 8-5: Distances between 3 ions involved in Mg-F chaining in FMgNaK at 800 °C. The figure only displays the period within a data range of 15-35 ps.

Figure 8-6: An example of Mg-F chaining observed at 750 °C. The third Mg²⁺ ion, Mg₉₂, was completely dissociated and did not participate in Mg-F chaining.

Figure 8-7: An example of a Mg monomer, observed in FMgNaK at 750 °C. It should be noted the simulation used in this figure is a separate simulation than that of Figure 8-6, though both were performed at 750 °C.
Figure 8-8. Snapshot of the simulation of the molten salt FMgNaK at 1073 K. This snapshot was taken 15 ps into the simulation. Fluoride ions are green, potassium ions are purple, sodium ions are blue, and magnesium ions are yellow. ........................................................ 81

Figure 8-9. Snapshot of the simulation of the molten salt FMgNaK at 1073 K. This snapshot was taken 40 ps into the simulation. Fluoride ions are green, potassium ions are purple, sodium ions are blue, and magnesium ions are yellow. ........................................................ 81

Figure 9-1. The total simulation energy in Hartrees (top) and the simulation liquid density (bottom) as functions of time for a simulation containing Mo(III) in FLiNaK at 500℃..... 89

Figure 9-2. Complexes formed by Mo of varying oxidation state in FLiNaK at 950K. Mo is blue and F is green............................................................ 92

Figure 9-3. Mo-F radial distribution functions for all mononuclear molybdenum complexes observed in FLiNaK at simulation temperatures of 950K (top). While the simulation cells analyzed here have an average box length of 10.6 Å, the smallest box has an average length of 10.2 Å, and so the RDFs are shown to a range of $r \leq 22(10.2 \text{ Å})$, or 7.2 Å (see section 2.3 above). For ease of interpretation, the region from 1.6 Å to 2.5 Å, encompassing the first peak, is shown in detail (bottom). ..................................................... 95

Figure 9-4. Molybdenum complexes observed in FLiNaK at 900°C in the presence of UF₄; U is yellow, Mo blue, F green. .................................................. 100

Figure 9-5. Molybdenum complexes observed in FLiNaK at 667°C (940K) in the presence of water. Mo is blue, F green, H white and O red. .................................................. 100

Figure 9-6. Molybdenum fluoro-oxides formed in FLiNaK at 940K (667°C):

  a) Mo(H₂O)F₅⁻²/MoOF₅⁻⁴, and b) MoO(OH)F₄⁻⁴/MoO₂F₃⁻⁴ before and after the hydrogen(s) on the hydroxide groups are taken by solvent ions. ......................................... 101
Figure 9-7. RDFs for Mo-O pairs in FLiNaK at 940K (667°C). The RDFs shown are for the MoF₅O⁴⁻ and the MoF₈O₂⁴⁻ complexes. The solid lines represent the RDFs generated using only the last 1 ps of simulation data, while the dashed lines represent the RDFs generated using the entire 10 ps of production run.

Figure 9-8. Overlaid simulation density distributions comparing the effects of planewave cutoff value sets. The average density with its 95% confidence interval is also shown for each distribution.

Figure 9-9. Overlaid simulation density distributions comparing the impact of the planewave cutoff value sets used in this work versus much higher cutoffs. The average density with its 95% confidence interval is also shown for each distribution.

Figure 9-10. The equilibration densities of two FLiNaK cells at 940K are shown, comparing the impact of including VdW corrections. An experimental correlation value is shown as well for reference.

Figure 9-11. MoF₆²⁻ in FLiBe at 727°C. The complex Bader charge is -2.38. This cell contained 66 F atoms, 28 Li atoms, 14 Be atoms, and 3 Mo atoms.

Figure 9-12. Mo₂F₈²⁻ complex in FLiBe at 500°C. The complex Bader charge is -1.91. This cell contained 62 F atoms, 14 Be atoms, 28 Li atoms, and 2 Mo atoms.

Figure 9-13. The mechanism of dinuclear formation involves two molybdenum hexafluoride mononuclears sharing a coordination fluoride ion.

Figure 9-14. Mo₂F₁₀⁴⁺ complex formed in FLiBe simulation cell at 727°C. The complex Bader charge is -3.56. This cell contained 66 F atoms, 28 Li atoms, 14 Be atoms, and 3 Mo atoms.
Figure 9-15. Molybdenum fluoride trinuclear complex observed in FLiBe at 667°C. The complex Bader charge is -2.95. This cell contains 66 F atoms, 14 Be atoms, 28 Li atoms, and 3 Mo atoms.

Figure 9-16. Molybdenum fluoride and uranium fluoride complexes observed in FLiBe at 727°C. The complex Bader charge on the dinuclear is -1.99 and on the mononuclear is -1.71. This cell contained 14 Be atoms, 78 F atoms, 28 Li atoms, 3 Mo atoms, and 3 U atoms.

Figure 9-17. RDFs for chloride pairs in KLiCl at 500°C. This cell contained 50 Cl atoms, 22 Li atoms, and 28 K atoms.

Figure 9-18. Mo_2Cl_8^{2-} complex found in KLiCl at 500°C.

Figure 9-19. A second Mo_2Cl_8^{2-} complex found in the same simulation cell as Figure 9-18. The chloride coordination around each molybdenum ion has increased by one in this restructure. The complex Bader charge is -1.867.

Figure 9-20. The RDFs for the Mo-Cl pair before and after the restructuring of the complex.

Figure 9-21. Mo_2Cl_{10}^{4-} complex found in KLiCl at 500°C. The complex Bader charge is -3.52.

Figure 10-1. Illustration of standard states for minor components in molten salt systems.

Figure 10-2. Schematic diagram of the electrochemical cell.

Figure 10-3. Infinite dilution linear fit on molality scale for CoCl_2 in NaCl-KCl at 1073 K. Data from Hamby fit to the theoretical slope of 2.303RT/nF rather than linear regression.
Figure 10-4. Infinite dilution linear fit on mole fraction scale for CoCl$_2$ in NaCl-KCl at 1073 K, compared to pure component standard potential for the same data. Data from Hamby$^{233}$ fit to the theoretical slope of $2.303RT/nF$.

Figure 10-5. Comparison of the activity coefficients calculated for CoCl$_2$ in NaCl-KCl by two different methods: (a) concentration on mole fraction scale, and (b) concentration on molality scale. The relationship between the concentration and the activity is shown in (b) for both standard states.

Figure 10-6. Infinite dilution linear fit on mole fraction scale for the electrochemical cells in Hamby$^{233}$ at 1073 K in various solvents. Data fit to the theoretical slope of $2.303RT/nF$ rather than linear regression. Left, (a) Co/Ag Cell. Right, (b) Ni/Ag Cell.

Figure 10-7. Visual representation of the Bader volume of the F$^-$ ion in (a) FLiBe and (b) FLiNaK. The figures are on the same scale for ease of comparison. Brown: K$^+$; yellow: Be$^{2+}$; green: F$^-$; blue: Na$^+$; purple: Li$^+$. 

Figure 10-8. Overall Bader Volumes of F$^-$ ions in FLiBe and FLiNaK at various temperatures.

Figure 10-9. Emf series vs temperature for LiCl-KCl using the infinite dilution standard state. Temperature between 650 K and 800 K. Reference: Ag(I)/Ag (0) in LiCl-KCl at infinite dilution.

Figure 10-10. RDF (fluoride density as a function of distance from the center of the cesium ion). (a) Raw RDF data. (b) Integral of RDF data.

Figure 11-1. Visualization of the initial configuration of each AIMD simulation. Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow. To illustrate.
periodic boundary conditions, mirror images of the bulk salt extend in the x and y-directions. ................................................................. 160

Figure 11-2. Cesium mass loss ratio over time in FLiBe at 800˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown. ....................... 163

Figure 11-3. Cesium mass loss ratio over time up to 24 hours in FLiBe at 800˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown........ 163

Figure 11-4. Cesium mass loss ratio over time in FLiBe at 650˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown. ..................... 164

Figure 11-5. Cesium mass loss ratio over time in FLiBe at 500˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown. The data shown at t = 0 was not included in the regression............................... 165

Figure 11-6. Radial Distribution Functions (RDFs) for Cs-Cs pairs in FLiBe at 500˚C, 650˚C, and 800˚C. A line has been added at g(r)=1 over the range 3.7-8.0 Å............... 167

Figure 11-7. Neighbor Functions for Cs-Cs pairs in FLiBe at 500˚C, 650˚C, and 800˚C. A line has been added for the normalized integral of (g(r)=1) over the range 3.7-8.0 Å...... 167

Figure 11-8. Visualization of an equilibrated AIMD simulation of CsF in FLiBe at 800˚C. Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow.......... 168

Figure 11-9. Average distance between all Cs-Cs pairs for each simulation temperature. A moving average was applied to the average distance between Cs-Cs pairs to clean up the data. The dotted black line indicates half of the simulations’ box length. Because all three simulations were run at different temperatures, the box lengths were slightly different, however the standard deviation between the three simulations’ box lengths was calculated at 0.061 Å. .............................................................................. 170
Figure 11-10. Visualization of an equilibrated AIMD simulation of CsF in FLiBe at 650°C.

Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow.................. 171

Figure 11-11. Visualization of an equilibrated AIMD simulation of CsF in FLiBe at 500°C.

Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow.................. 172

Figure 12-1. The mean distance to homoelemental neighbours (MDH) for FLiNaK

constituents in a simulation at 873K................................................................. 178

Figure 12-2. The potential energy of simulations of FLiNaK at 873K containing 2 H atoms

and 1 O atom. ........................................................................................................... 179

Figure 12-3. The mean distance to homoelemental neighbours (MDH) for FLiNaK with

H₂O elemental constituents in a simulation at 873K................................................ 180

Figure 12-4. Initial positioning of Ni and H₂O in the simulation at 873 K with 1.75 Å of

Ni-O spacing. The bulk salt is shown as faded for context........................................ 181

Figure 12-5. Ni-O chain formation within molten FLiNaK at 873 K in the presence of

excess HF.................................................................................................................. 182

Figure 12-6. Ni-O structure observed in FLiNaK at 873 K in the presence of excess HF.

The HF structures are also accented, but the bulk salt cations and any F⁻ ion great than

2 Angstroms from an H⁺ ion are faded................................................................. 183

Figure 12-7. Bader volumes for 2 F⁻ ions are shown enveloping an F-H-F complex in

molten FLiNaK at 873 K................................................................. 183

Figure 12-8. The mean distance to homoelemental neighbours (MDH) for FLiNaK with

Ni, O, and H elemental constituents in a simulation at 873K................................. 184
1 INTRODUCTION

The aim of this research is to develop the capabilities to accurately predict the behavior of molten salt mixtures.

When we say we wish to predict a molten salts behavior, we mean three things primarily. First, we want to know the basic thermophysical properties of molten salt mixtures. Second, we want to know what ionic complexes form. Third, we want to predict how adding another trace contaminate will alter these properties and complexes, at least at a basic level.

The molten salt nuclear reactor (MSR) offers potentially immense economical, infrastructural, and medical benefits. The MSR produces affordable and reliable energy as well as valuable isotopes with life-saving medical applications, all while addressing the three grand challenges of nuclear technology: (1) safety, (2) non-proliferation, and (3) waste disposal. While a small MSR was constructed and briefly operated at Oak Ridge National Lab several decades ago, many design challenges must be overcome before an updated MSR can be designed, licensed under current U.S. federal regulations, and eventually operated safely and economically. One such issue is knowing how a molten salt with radioactive contaminate will behave in a fluid system. These contaminate will form various solution complexes which may interact with one another, leave solution, or alter thermodynamic properties of the molten salt, which will in turn affect behaviors such as flow and heat transfer.
Ab initio molecular dynamics (AIMD) simulations are an effective tool for exploring solute-solute and solute-solvent interactions within molten salts.

Achieving these three goals will grant us power in designing the MSR. Besides basic neutronics considerations, knowledge of thermophysical properties and complexations will allow reactor designers to account for supporting features, such as pumping power requirements, heat exchanger sizing, corrosion resistance, and even various separation techniques\(^5\). Furthermore, understanding the general patterns of behavior change will allow us a greater range of safe reactor control.

In order to design safe, effective molten salt reactors, designers must know the thermophysical properties of molten salts and how those properties change as other chemicals such as fuel, fission, and corrosion products are added\(^6\). We do not know much about the properties of the molten salts being considered for MSR design\(^7\). We know even less about how those properties will change as fission products and corroded particles accumulate in the molten salt\(^8\). Many are currently experimenting on molten salt mixtures to determine these properties, but the number of experiments needed is tremendous. Experimental work is difficult and costly, as material acquisition and safe handling of radioactive chemicals in high temperature molten salts is not simple. If researchers supplement experimental work with computational chemistry, much time, money, and effort may be saved.

It is also important to know where dangerous or valuable species will be found in the system, and in what form. For example, if Molybdenum-99, a rare, radioactive isotope used to make a medical imaging isotope (Tc-99m), is to be harvested from the reactor, we must know where to find it. It could form a fluoride vapor product, or complex with other molybdenum in solution, or freeze onto certain nickel-alloys. We need to know what each such solute will do in
solution, and computational approaches allow the direct prediction of solute behavior from quantum mechanics.

While mapping out the entire network of potential permutations of solute-solute impacts over all possible concentrations is beyond the scope of this work, a key objective of this research is demonstrating that experimental behavioral predictions can be made from qualitative observations of phenomena in AIMD.

Significant achievement in each of these three goals has been accomplished and is examined in this work.
2 MOTIVATIONS TO UNDERSTAND MOLTEN SALT SOLVATION CHARACTERISTICS

2.1 The First Motivation: Targeted Alpha Therapy

2.1.1 Targeted Alpha Therapy Background

Targeted α-particle therapy (TAT) is an effective treatment for many cancers\(^9\). In this treatment, a radioactive isotope is attached to a particular protein antibody and injected into the patient\(^{10}\). The protein selectively locates the tumor cells, and the radioisotope undergoes a high-energy, α-particle emission, destroying the walls of the tumor cell without the extensive collateral damage caused in many mainstream cancer treatments such as chemotherapy\(^9\). This technique is highly effective, especially against smaller-volume tumors\(^9\). In 1996, a study was conducted with 18 patients with myeloid leukemia\(^{11}\). 15 of the patients had leukemic blasts, or immature white blood cells spilling out of the bone, in the peripheral blood around the leukemic bone tissue\(^{11}\), and 14 of those 15 experienced a reduction in the circulating blast. The average and median reduction in blast was 90% and 98.5% respectively\(^{11}\). 14 of the 18 patients also had clear reductions in bone marrow leukemia cell count within 7 to 10 days\(^{11}\).

The 1996 study and many subsequent studies have all concluded two things: TAT is very effective against certain cancers including leukemia and we cannot implement it at present\(^9{\text{-}}^{13}\). The common reason being that the radioisotope from the study, bismuth-213, just isn’t available\(^{12}\). But we can fix that.
2.1.2 **Bismuth-213 Generation**

Bismuth-213 (Bi-213) is a radioactive material. It is unstable, with a half-life of 46 minutes. This short half-life means Bi-213 cannot be appreciably acquired through mining. Bi-213 can be produced by radioactive decay of other radioisotopes. When a radioisotope undergoes $\alpha$-emission, a daughter isotope is formed by the loss of the $\alpha$-particle. The daughter product has two less neutrons and two less protons. Thus, Bi-213 is formed by the $\alpha$-particle emission of At-217, which is formed by the $\alpha$-particle emission of Fr-221, and so on up the chain. We must find a quasi-stable parent isotope supply, and then we will have a supply of Bi-213. Ac-225, the parent isotope of Fr-221, has a half-life of 10 days, which is large enough for feasible distribution. However, Ac-225 is also not readily available in nature. Ac-225 can be made as a decay product of uranium-233. If we were able to rapidly separate out Ac from U-233 and its other decay products, we could then procure a steady supply of Bi-213 for TAT doses.

Nuclear decay reactions are independent of position, physical conditions, and the composition of neighbouring atoms; they simply occur. In a solid U-233 sample, you would find the Ac-225 randomly distributed throughout the highly radioactive U-233. Thus separation processes of nuclear decay products are typically more facile in liquid or vapour phases, where the decay products are not physically entrapped within the parent isotope. A U-233 sample dissolved in a liquid system would then allow decay products to be formed in situ and already be chemically distinct from other elements. A plausible liquid solvent family is molten halide salts, which have been shown to solvate uranium halides well.

U-233 is not the uranium commonly used in nuclear applications today, however chemically it behaves identically to all other U isotopes. We can thus consider them...
concurrently. U-235 is of special interest, as this is the isotope used historically in fission reactors. A discussion of the history of nuclear energy will add valuable context to our current discussion.

2.2 The Second Motivation: Improved Nuclear Energy

We will enable a discussion of amassing U-233 by first discussing why there is no U-233 amassed already. This requires a brief overview of the nuclear energy field in the United States today.

2.2.1 An Overview of Nuclear Energy in the United States of America

Nuclear energy is just one way mankind harnesses available energy sources to produce usable energy. Radioactive elements exist naturally throughout the entire earth. These elements eventually decay, and that decay often involves a heat release. Sometimes these elements decay very quickly, and sometimes they decay very slowly, over millions of years. Nuclear energy uses the heat generated by certain decays to produce electrical energy in a power generation cycle. Nuclear energy does not include some kind of unholy science to monstrously alter any element. Nuclear energy simply harnesses energy releases that occur in nature, just like wind energy, or solar energy.

In the United States, there are almost 100 commercially operating nuclear reactors. Each of these utilizes the energy release due to fission of Uranium-235 to heat highly pressurized water. The water is used to superheat another water loop, and the steam is pushed through turbines to generate power. U-235 can be highly concentrated for use in nuclear weapons, so many safeguards exist to prevent nuclear energy system components from being weaponized. Even without concentrating enough fissile material to create an explosion, fissile materials can
still undergo supercritical nuclear reactions, which can result in areas being left uninhabitable for decades, like the Chernobyl Unit 4 accident. Legislation is the predominate safeguard against nuclear accident \textsuperscript{20}.

Nuclear energy is difficult to license. The word nuclear (sometimes pronounced nü-kü-lar) conjures mental images of explosions, wastelands, and horrific mutations for many people. Weaponized nuclear technology has a truly awful capacity for destruction. The Government protects this nation by strictly monitoring the usage and distribution of fissile material, just like it monitors the distribution of chemicals that can be used to make bombs or bio-weapons \textsuperscript{21}. The Nuclear Regulatory Commission (NRC) must license any entity wishing to build and operate a nuclear power plant. The NRC only grants a license to an applicant if the plant design meets all applicable regulations. The NRC investigates the characteristics of the proposed site, including nearby human populations, seismology, geology, meteorology and hydrology \textsuperscript{21}. The NRC also investigates the plant design, the hypothetical accident responses, the qualifications of any operators, and any environmental discharges or impacts \textsuperscript{21}. This exacting licensing process curtails many plans to create new nuclear power plants and drives up the price of any reactors actually built. The last new reactor has two units which were licensed in the United States of America in 1995\textsuperscript{22} and 2015\textsuperscript{19}.

Uranium-233 is not licensed to be appreciably present in US nuclear reactors. In order to license a reactor design featuring U-233, the proposed reactor design would need proof of safety under every imaginable situation, including being struck by a commercial airplane \textsuperscript{20}. This safety can be shown in large part using typical operating data. The Catch-22 that arises is that you cannot license a U-233 reactor without operating data, and you cannot operate a U-233 reactor without a license \textsuperscript{23}. 
Economics is another major factor in the lack of new reactor construction. Building a new reactor today costs 300% more than just a few years ago, because of increasingly stringent safety protocols\textsuperscript{24}.

These and other factors dim the prospect of just happening upon a steady source of U-233 decay products.

All is not yet lost. Many researchers suggest that smaller reactors could reasonably offset the licensing challenges and economic hurdles of large nuclear reactors\textsuperscript{21, 25, 26}. A Small Modular Reactor (SMR) is not just a viable alternative, but a sound stepping stone in generating reactor operation data\textsuperscript{21}. Two possible designs for a small modular reactor that utilize salt are the molten salt reactor (MSR) and the fluoride-salt cooled, high-temperature reactor (FHR).

### 2.2.2 The Molten Salt Nuclear Reactor

Access to usable energy is vital to the thriving of individuals and nations. Nuclear energy is one way mankind has found to harness energy sources that exist in nature (in this case, radioactive elements within the earth) to produce usable, useful energy. However, this form of energy is not without drawbacks. The three largest issues with producing nuclear energy are 1) guaranteeing safety, 2) non-proliferation of nuclear weapons, and 3) proper disposal of nuclear waste, and the costs of addressing these important issues are a major reason that traditional nuclear power is becoming unprofitable compared to other sources of electricity. If nuclear energy is to contribute to a thriving future, engineers and scientists must develop new reactor types which address the major drawbacks of nuclear power while also providing useful and profitable applications beyond electricity generation alone.
One such reactor type is the molten salt reactor (MSR). A molten salt reactor solvates fission materials in a salt solvent, as opposed to solid fuel-rods cooled by water as in traditional reactors. The fluid pools in the reactor core, and the smaller pipe diameters elsewhere in the system make the reactor core the only section of the reactor able to sustain a fission reaction. An MSR can also utilize alternative fuel isotopes such as U-233 (produced from thorium) in lieu of the U-235 used in traditional reactors. These features allow an MSR utilizing thorium fuel to address the three main issues of nuclear energy:

1) Molten salt reactors allow for inherent and passive safety systems, rather than the more active systems needed for solid-fuel reactors. Active safety systems in solid-fuel reactors are to prevent core meltdowns. If the fuel rod is compromised in a meltdown incident, molten fuel and cladding will leak into and pool at the bottom of the reactor. If the quantity of fuel per volume becomes high enough, a supercritical nuclear reaction will ensue. This is frowned upon. In the MSR, the fuel is soluble and well-mixed in the solvent salt. The molten salt expands as temperature increases, reducing criticality. Also due to the very high normal boiling points of the solvent salts, the reactor can be operated at atmospheric pressure, instead of the 14 GPa used in light water reactors to prevent the boiling of water in the core. This all but eliminates the risk of pressurized explosions, especially hydrogen explosions.

2) Using U-233 in lieu of U-235 invariably introduces trace amounts of U-232, a highly radioactive gamma radiation source. The presence of U-232 combined with the lack of high local concentrations of U-233 make weaponizing the MSR or its components considerably more difficult than U-235 or one of its by-products, Pu-239.
3) Molten salt reactors can be designed to produce valuable isotopes while nearly eliminating production of transuranic wastes. The valuable isotopes can be continuously separated out of the reactor and subsequently vended. Even if the process of licensing a molten salt reactor that utilizes U-233 as the fuel is too daunting, a molten salt reactor with U-235 fuel is also quite beneficial. As mentioned above, any SMR will be more economically feasible than a full-sized traditional power reactor, and the MSR is no exception. The MSR design can be operated at atmospheric pressure, and that opens the possibility of removing the most expensive part of the traditional reactor design: the containment barrier.

The molten salt reactor design was originally built in Oak Ridge National Laboratory, and was operated from 1965-1969. I spoke with Sydney Ball, an operator of the original MSR who still resides here in Oak Ridge, and he told me that he was tasked with driving the MSR into operating regions of instability, and he was never able to do so. This is the kind of nuclear energy that can enable the world’s transition to clean energy.

2.3 The Third Motivation: Molten Salts in Thermodynamic Cycles

Molten halides salts have high melting temperatures, but also high heat capacities. Even if the nuclear fuel is not directly dissolved in the salt, molten salts can be useful as coolants in the power generation cycle. Fluoride salts are of particular interest as high-temperature nuclear reactor coolants. A design featuring a fluoride salt coolant of a nuclear pebble-bed style reactor is the fluoride-cooled high-temperature reactor. However, even in a system that does not solvate fuel directly, vessel corrosion and fuel pebble life are important safety and viability considerations.
2.4 Additional Motivations: Molybdenum-99 and Other Rare Isotopes

Nuclear reactors can also produce more than electrical energy, such as rare isotopes. When considering the economics of nuclear technology, it is prudent to consider the vending of valuable by-products.

2.4.1 One Man’s Trash: The Market for Fission Products

Nuclear reactions can yield priceless commodities. We have already discussed the potential of Bi-213 in oncological applications. When uranium undergoes fission, a rich plethora of isotopes are created, such as several rare-earth metals. Rare-earth metals are often used in cell phones, computers, and electric cars. They enable electrical and magnetic technologies to be smaller, lighter, and faster. Many of these rare-earths are not naturally abundant, so isolating them in a reactor would be a lucrative bonus.

Molybdenum-99 (Mo-99) is another fission product of uranium. Mo-99 is used in almost all nuclear medicine imaging, but has a half-life of just 66 hours. These medical imaging procedures include MRI scans and are used to detect cancers and for other diagnostics. As of 2020, no Mo-99 was produced and distributed in the United States.

It will be easier to obtain Mo-99 than Bi-213. In a small nuclear reactor containing U-233, both fission products and decay products will be observed. The decay products, namely our source for Bi-213, will be much less abundant than the fission products. Ac-225 will be so dilute, it cannot be appreciably concentrated. Mo-99 will reach a high enough concentration that it can be theoretically separated out of the reactor.
Mo-99 has a high fiscal value. In 2009, the cost of Mo-99 production was valued at $25 Million USD per gram of Mo-99 \(^{36}\). If the Mo-99 produced in a U-233 reactor could be separated out and sold, the costs of the reactor could be greatly offset and even overcome.

Molybdenum-99 production and isolation is a viable path to licensing a large U-233 reactor for bismuth-213 production. As previously mentioned, smaller reactors with smaller hazards and potential consequences are easier to license. So rather than attempt to license a full-sized nuclear power reactor with U-233, one could start by building a small U-233 (or U-235) reactor designed to produce valuable medical isotopes, especially Mo-99. This small medical reactor would create essential data on molten salt reactor operation needed for the licensing of a larger reactor, while the steady supply of Mo-99 would provide funding for the construction of a larger reactor. Once a larger U-233 reactor is commissioned, a rich supply of Bi-213 can be harvested.

### 2.4.2 Continuous Separation

Isolating short-lived products requires a continuous process. Since Mo-99 has a half-life of only 66 hours, it needs to be extracted from a reactor as quickly as possible. In a traditional U-235 light water reactor (LWR) in the United States, the normal shut-down and fuel rod removal procedure can take days, and in that time, reactor operation (and therefore fission product creation) has stopped. It can take several more days to fully power-on a reactor. Current reactors also use a solid fuel, meaning you would need to chop apart your U-235 fuel pellets to try to isolate these fast-decaying fission products. This seems a tad impractical. A better alternative would be a reactor design in which the fuel and fission products were solvated, or at least not constrained in fuel rods. This would allow for a continuous separations process, which could be executed while the reactor is operating\(^{28}\).
The Molten Salt Reactor (MSR) is an alternative to the nuclear reactors operating in the U.S. today. The MSR is not a new idea, and was originally tested in the 1960s\(^2^7\). The reactor design differs from operating reactors in that the fissionable fuel is solvated in a liquid salt. The salt is circulated through a reactor and is allowed to pool in the reactor core, enabling local criticality, or sustained fission. The salt is then passed through a processing system to separate out fission products and replenish lost fuel so that concentrations of solutes in the salt remain constant. The MSR fills the requirement that the separations process can be conducted during reactor operation. The FHR design also allows for online refueling and thus online separation.

### 2.4.3 Economic Feasibility

The MSR and FHR designs have several features that contribute to economic feasibility. Two of the largest costs of conventional reactors are safety features and waste disposal. Molten salt designs are less subject to the causes of these costs.

Nuclear reactors must be walk-away safe, meaning that plant safety protocols must not depend on any active human control\(^2^0, 2^1\). Current LWR designs have difficulty meeting this requirement; current reactor designs pump water through the core. In a power failure, the water stops circulating, and the fuel will continue to decay, releasing heat into the highly pressurized but stagnant water. Eventually the fuels become hot enough to liquefy. This is called a meltdown, and results in uncontrolled nuclear fission, which in turn results in extreme power releases into the water. The water heats up, boils, and eventually disassociates into hydrogen and oxygen gases. A single ignition source is all that it takes to create a hydrogen explosion. This was the case in Fukushima in 2011\(^3^8\). Utilizing multiple redundant safety systems is the current solution to the issue of power failures and other catastrophes. This leads to reactors costing billions of dollars, and needing decades to be profitable\(^2^4\).
The molten salt reactor design relies on passive safety\textsuperscript{39}. Because the fuel is already solvated in the molten salt, a meltdown cannot happen\textsuperscript{27}. In the event of power loss and temperature spikes, a plug at the bottom of the reactor made of a different salt will melt, and drain the core into holding tanks that will diffuse the fuel concentrations, cooling the salt\textsuperscript{40}. This greatly reduces the amount and redundancy of necessary safety systems\textsuperscript{39}. The MSR also operates at atmospheric pressure, rather than the high pressures found in our current reactors, which greatly reduces the cost of materials used to contain the reactor. The containment shell is consistently among the most expensive components of the LWR design. The FHR can also operate at atmospheric pressure\textsuperscript{26}.

Nuclear reactors featuring U-235 and U-238 create many less-desirable products via neutron absorption that does not result in fission. Some of these absorption products have very long half-lives and are called transuranic wastes. Typically, a spent fuel rod has a veritable smorgasbord of these wastes within it, and due to the high collective radioactivity, there are relatively few ways to deal with it. A vast amount of debate over nuclear energy is centered on how to deal with the waste products.

A reactor that features U-233 is far less likely to create absorption products or transuranic wastes, instead favoring the smaller radionuclide products such as Bi-213. You know, the ones we wanted in the first place. Additionally, a continuous separation process would facilitate the potential isolation of all products. Many of the products created in an MSR are vendible, such as Mo-99.

In addition to reduced start-up and waste management costs, the cost of electricity produced by the MSR was reduced 7.3\% compared to our current reactors and 9.5\% compared to coal plants\textsuperscript{41}.
The MSR features additional benefits beyond improved safety and economics. Salts often sport high moderating ratios, making them ideal moderators from a neutronics standpoint\textsuperscript{42}. Salts also tend to have high heat capacities and high densities, which improves the thermodynamic efficiency of the power generation cycle\textsuperscript{42}. The MSR design also operates in the thermal region of fission reactions, meaning it requires as little as 10\% of the fissile material of our current reactors to obtain the same power generation\textsuperscript{40}.

2.5 The Common Challenges

All the above motivations share some common challenges. Because they each involve nuclear technology, they each must be licensed under the 10\textsuperscript{th} Code of Federal Regulations\textsuperscript{21}. The MSR must be understood to be licensed by the NRC to operate. As with any nuclear technology, strict regulations exist to ensure safety and to minimize risk. The MSR must comply with these regulations. MSR designers aiming to comply must understand how the MSR and its components will behave in a variety of circumstances. If a designer wants to design a molten salt reactor, he or she must be able to predict the behavior of the molten salt in the system. If that designer wants to predict molten salt behavior, he or she must know the properties of the salts at a multitude of operating conditions, and how those properties change as other chemicals are added to the salt\textsuperscript{6}.

Many properties are important when designing a molten salt reactor. We must know how the neutronics in the core will occur to design the fuel requirements. We must know how the fluid salt will corrode its surroundings to design the wall and units in the system. We must know how the salt can be pumped, piped, and mixed to design the plumbing around the core and in the separations system. We must know how the solutes in the molten salt can be separated out to
obtain the valuable products Mo-99, Ac-225, and others. We must know what happens when
the salt freezes due to power loss. These and many other behaviors must be understood.

An analogy is found in water. Scientists and engineers know how pure water will behave
at certain conditions. No one is surprised when pure water freezes at 0°C. People understand
that while swimming in pure water, you may sink. If you add a solute, such as table salt, to the
pure water, the properties of water begin to change. Salt impurities lower the freezing point, alter
the electrical conductivity, and even change the density. The Dead Sea provides an excellent
example of this density change; the increased density of the water-and-salt mixture makes
sinking your body into the sea much more of a chore.

In order to design safe, effective molten salt reactors, designers must know the
thermophysical properties of molten salts and how those properties change as other chemicals
such as fuel, fission, and corrosion products are added. We do not know much about the
properties of the molten salts being considered for MSR design. We know even less about how
those properties will change as fission products and corroded particles accumulate in the molten
salt. Many are currently experimenting on molten salt mixtures to determine these properties,
but the number of experiments needed is tremendous. Experimental work is difficult
and costly, as material acquisition and safe handling of radioactive chemicals in high temperature
molten salts is not simple. If researchers supplement experimental work with computational
chemistry, much time, money, and effort may be saved.

It is also important to know where dangerous or valuable species will be found in the
system, and in what form. For example, if molybdenum-99, a rare, radioactive isotope used to
make a medical imaging isotope, is to be harvested from the reactor, we must know where to
find it. It could form a fluoride vapor product, or complex with other molybdenum in solution, or
freeze onto certain nickel-alloys. We need to know what each such solute will do in solution, and computational approaches allow the direct prediction of solute behavior from quantum mechanics.
3 MOTIVATIONS TO STUDY MOLTEN SALT CHEMISTRY USING AB INITIO MOLECULAR DYNAMICS

3.1 The Experimental Predicament

Experimental work in molten salts is relatively expensive, as material acquisition and safe handling for radioactive chemicals in high temperature molten salts is not trivial\textsuperscript{31, 52}. There is a limitless number of experimental conditions that could be tested. Limitless testing is unfeasible. You might also find it rather dull. Testing the properties of a molten salt requires equipment that can stand temperatures of well over 1000 K\textsuperscript{31}. Certain viable salts contain elements such as Beryllium (Be) that are highly toxic and require expensive safety protocols. Radioactive materials require many of their own safe-handling standards. These factors do not prohibit experimental measurements of the thermophysical properties of molten salts, but they contribute to the costs of such empirical work\textsuperscript{43}. The costs of time and money constrain the amount of empirical data that can be collected. If researchers supplement experimental work with computational chemistry, much time, research effort, and financial funding is saved.

A theory-based supplement to experimental work enriches the data set\textsuperscript{48}. Experimental and computational findings are complementary supports of the same conclusion. Validation fosters confidence in conclusions, especially where nuclear technology is concerned. Some theoretical findings, such as complex structure or oxidation state, can enable insights on plausible operations and separations techniques\textsuperscript{53, 54}. The scope of empirical work is refined by
the findings of theoretical work\textsuperscript{55}. A narrower experimental focus allows for a better return on research resources invested. The simulation work conducted under this prospectus will supplement, validate, add insight and focus the aims of the experimental work conducted elsewhere. The experimental results will likewise vindicate the results of this theoretical work. Work without empirical base is often subject to skepticism, especially in the nuclear power industry. Therefore, sense and economics mandate computational work on molten salt properties be done. This sort of theoretically-based computational work is called molecular dynamics (MD) simulations\textsuperscript{56, 57}.

3.2 Molecular Dynamics Simulations

Molecular dynamics (MD) simulations are a powerful computational chemistry tool. These simulations model the energy and forces between atoms in order to predict the behavior of a system of atoms over time. In addition to allowing researchers to visualize how atomistic interactions occur, MD can predict chemistry and material properties with complete safety and relatively low cost, which is particularly useful for experimentally tricky materials such as molten salts.

However, studying molten salts through MD is not straightforward as very few interatomic potential models exist for these salt systems. An interatomic potential model, or force field, is a mathematical model used to calculate the potential energy between atoms in a system. Force fields must be independently parameterized for any given chemical system (e.g., an F\textsuperscript{-} anion in aqueous solution will require different parameters than an F\textsuperscript{-} anion in a molten fluoride salt), and different force fields may be more or less successful at producing MD simulations that accurately predict various chemical behaviors and properties.
One model derived specifically for solid alkali halides is the Born-Mayer-Huggins potential model\textsuperscript{58-61}. This model was later adapted to include repulsion damping terms based upon the work of Fumi and Tosi\textsuperscript{62}. It has been shown that all models dealing with polarizable ions or dipoles should include a potential term to account for the energy needed to distort a molecule to its polarized state\textsuperscript{63}. Polarization is an important consideration for MD of molten salts,\textsuperscript{64, 65} especially as strong Coulombic interactions between like-cations are screened by the polarization of the anions\textsuperscript{66}. Models for molten salts allow for dipole and even quadrupole polarizations in interatomic interactions within molecular dynamics\textsuperscript{67-69}. Such polarizable models, based on AIMD electronic calculations drastically improve the transferability of the potential parameters\textsuperscript{70, 71}. Including many-body effects and ion compression and deformation further improves model accuracy and transferability\textsuperscript{72}. Finally, dispersion interactions should also be included in the interaction potential model, which is important when simulating phase changes in MD\textsuperscript{73}.

Models including these features have been tested with some salts including FLiBe (66.7-33.3 mol\% LiF-BeF\textsubscript{2}), FLiNaK (46.5-11.5-42 mol\% LiF-NaF-KF) and KLiCl (55.8-44.2 mol\% LiCl-KCl), and the resulting properties calculated were compared to existing experimental data\textsuperscript{6, 50, 74, 75}. The results of these studies show strong agreement to experimental data across most properties, but the data is still fairly limited in temperature range and composition\textsuperscript{6, 57, 74, 75}. Furthermore, we would like to consider a less-studied salt, FMgNaK (34.5-59.0-6.5 NaF-KF-MgF\textsubscript{2} mol\%). FMgNaK is considerably more affordable and safer to work with than salts such as FLiBe, while still being serviceable neutronically. We will also study a few key solutes, such as the aforementioned molybdenum-99. No MD potential models have been published for FMgNaK or for several of the solutes of interest in any salt. This is largely because FMgNaK
requires temperatures higher temperatures than were feasible in the original MSR Experiment (MSRE), and was thus passed over in favor of salts such as FLiBE and FLiNaK, which have remained more keenly in the MSR community’s conscious.

Potential parameters for a given MD potential model can be generated from fitting data created using ab initio simulations based on quantum mechanics\textsuperscript{68, 76}. In 1993 a technique was devised to match the forces computed in an first-principles molecular dynamics simulation with an MD simulation of the same system\textsuperscript{77}. In other words, we look at the forces created in a first-principles simulation of a given box of atoms at a given temperature, pressure, and configuration, and we ask, “What must the interatomic potential parameters be to create the same forces in the same box using MD?” We then generate the potential parameters and adjust them to minimize the differences between the forces computed by the two methods via an objective function\textsuperscript{77}. Other techniques and improvements have also been reported\textsuperscript{78-81}. Ercolessi reports that parameter transferability, and by extension predictive power, is impacted by the simulation database size and diversity\textsuperscript{77}. This means that the more AIMD simulations we have at various conditions, compositions, and sizes, the more powerfully predictive our potential models will be\textsuperscript{78, 82}. Our generating copious amounts of first-principles molecular dynamics simulation data via a software called CP2K will also add considerable statistical significance to the MD-predicted thermophysical properties of the molten salt mixtures\textsuperscript{75, 83}. Much work has been done on deriving methods for creating transferable interatomic potentials from ab initio calculations for molten salts\textsuperscript{83-89}. A key conclusion from this body of work is that transferability is intrinsically linked to polarizability. One of our goals is to simulate enough of the pure salts to create potentials that transfer well from one set of conditions to another. This will allow us to model molten salt behavior over a wide range of conditions, rather than only at a few select points.
Perhaps the largest benefit of using first-principles molecular dynamics simulation techniques is the insights directly into molten salt chemistry that a more theoretically based approach yields.

### 3.3 Ab Initio Molecular Dynamics Simulations

Ab initio molecular dynamics (AIMD) simulations, or first-principles simulations, can be used to predict molten salt behavior without the need for pre-existing interatomic potential models. Rather than modeling the interaction energy between atoms with a specifically parameterized force field, AIMD calculates interaction energy by solving an approximation of Schrödinger’s equation using density functional theory (DFT), a computational quantum mechanical modelling method. Using DFT allows us to treat atoms’ electrons as a fine 3D-grid of scalar charge values over the volume of the entire many-body system. AIMD thus allows the transfer of electrons and the breaking and forming of chemical bonds which allows the solutes we simulate to react and complex. Electron transfer reactions or redox reactions, which by nature are not feasible in classical MD simulations, can be simulated in AIMD. Using our molybdenum-99 example from before, if we can show that molybdenum readily reacts with fluoride to form a compound such as MoF₅, which is known to be a volatile above 500°C¹⁷, we can predict where it will accumulate in the reactor.

The advantages of first-principles simulation come at a cost, however, as AIMD is much more computationally expensive than classical MD using force fields and is therefore typically used for much smaller systems with smaller numbers of atoms and shorter simulation times. This means that there are some thermophysical properties that cannot be calculated using AIMD simulations because these properties require system sizes, gradients, or time scales that are too
large. Thus, viscosity, thermal conductivity, and heat capacity will be determined using molecular dynamics. Computational methods for these properties will be discussed below.

While AIMD simulations do not require interatomic potential models specifically developed for a given chemical system, they do utilize pseudopotentials. Pseudopotentials are an attempt to simplify the electronic wavefunction by assuming that only valence electrons will interact with the electrons of other atoms, affecting the overall electron density of the system. The non-valence or core electrons, on the other hand, are treated as a fixed density function around each atom nucleus, greatly reducing the complexity of the calculations that must be performed at each timestep.

Developing accurate pseudopotentials is especially difficult for heavier elements such as uranium, other fission fuels, and some fission products. Uranium, for example, contains valence electrons in the f-shell orbital, which means an accurate pseudopotential must allow those electrons to interact with the overall electron density of the system. (For reference, the orbital shells available to electrons in order of increasing size and complexity are s, p, d, and f.) For most ions, we will be using the standard Goedecker-Teter-Hutter pseudopotentials\textsuperscript{90}, but a more recent study on uranium reported pseudopotential values found to be more accurate\textsuperscript{91}.

As noted above, this project will use AIMD simulations to generate a data set needed to force-fit parameters for a classical MD model, allowing the computation of properties requiring larger-scale simulations for accurate statistics. However, there are several properties that are accessible within AIMD’s computational limits. These include density, diffusion coefficients, Bader charge and volume, salt and complex structure, and activity and solute-solute interaction impacts on activity coefficients. Methods for calculating these properties from AIMD are discussed below.
4 THERMOPHYSICAL PROPERTIES AND STRUCTURAL CHARACTERISTICS

4.1 Properties and Characteristics to be Predicted from AIMD

4.1.1 Salt Structure

Characterizing salt structure is important because when composition changes to the salt result in new structural networks, a sudden shift occurs in transport property values. For example, the viscosity of beryllium-difluoride is impractically high, but is greatly reduced by the addition of lithium-fluoride, creating FLiBe. We now understand the network changes that link composition to viscosity in FLiBe. Similar networks affects have been observed in conjunction with thorium-fluoride complexes. Composition-dependent networks affect other thermophysical properties, such as thermal conductivity. Magnesium fluoride is also known to behave differently than other fluoride salts, and an investigation into the structure of FMgNaK may shed light on why.

Radial distribution functions (RDF) are a convenient method for quantitatively describing salt structure. An RDF reports the normalized number of atoms of a certain species found within a shell of given radii around atoms of another species. Integration over the first peak of an RDF results in a coordination number. As early as 1972, RDFs have been used in the analysis of molten salts. RDFs can also be created based on x-ray diffraction studies. In recent years, AIMD has become a staple of RDF generation for molten salts.
4.1.2 Density

The density of a molten salt is needed to design basic fluid systems such as reactor pumps and piping. Density is also a convenient property to use for validating AIMD methodology, as it can be calculated from MD very straightforwardly compared to other properties, and because several salts such as FLiBe and FLiNaK have established experimental values of density in the literature\(^95\). A simple method of predicting densities from MD is to perform a simulation in the NPT ensemble (a fixed number of atoms at a fixed pressure and temperature). From the starting point, the simulation cell volume will fluctuate, eventually reaching equilibrium. Averaging the volume of this equilibrated cell over a sufficient period of simulation time gives an equilibrium volume \(V\). Density can then be calculated from this volume and the total mass of atoms in the simulation cell \(m\):

\[
\rho = \frac{m}{V}
\]  

(4-1)

4.1.3 Diffusion Coefficients

Diffusion coefficients are used in designing electrochemical separations processes to determine mass transport limitations, among other things. Calculating diffusion coefficients may be useful for validating AIMD simulations as it is a dynamic property (whereas density is a structural property), and diffusion coefficients that align with experimental values would indicate that simulations are properly capturing salt dynamics as well as structure. Such empirical data exists for pure FLiBe and FLiNaK\(^{52,100}\). Multiple research groups have used AIMD simulations to predict diffusion coefficients for several pure salts and a few solutes within those salts\(^{54,55,57,99,101-103}\). However, no data exists on FMgNaK nor on the solutes Mo-99 or Ac-225. Self-diffusion coefficients can be calculated from relatively small simulation cells, and so can be
found relatively reliably from AIMD\textsuperscript{98}. Self-diffusion coefficients can be calculated from the Einstein relation\textsuperscript{101}, as given in equation 4-24-24-24-2.

\[
D_i = \lim_{t \to \infty} \frac{1}{6t} \langle |r_i(0) - r_i(t)|^2 \rangle
\]

(4-2)

Where \(D_i\) is the diffusion rate of species \(i\), \(r_i\) is the position of ion \(i\), and the angled brackets denote the average value over all ions of species \(i\).

4.1.4 Bader Charge

Bader charges are an approximation of atomic contributions to electron charge density\textsuperscript{104}.\textsuperscript{105} A Bader cell is a volume of the electron density around an atom that is assigned to that atom using the Henkelman partitioning scheme of the electron density grid\textsuperscript{104}. The summation of the discrete charges of all points in a Bader cell yields the Bader charge, or an approximation of the actual charge of an ion. This has the advantage that our simulated ions will more closely approximate the charge of monatomic ions in a molten salt, because that charge is not always an integer value\textsuperscript{106}. The charge distribution at a point \(r\) within a unit cell can be approximated by

\[
\rho = N \int \psi^*(x; X)\psi(x; X) d\tau'
\]

(4-3)

Where \(N\) is the number of electrons, \(\tau'\) denotes the spin coordinates of all the electrons and the Cartesian coordinates of all the electrons but one, and \(\psi(x; X)\) is a solution to the stationary-state Schrödinger’s equation for a fixed arrangement of the nuclei\textsuperscript{105}. The charge distribution densities are assigned to a nuclei using a steepest-ascent method of a grid representation of the electron density\textsuperscript{104}, as proposed by Bader\textsuperscript{105}. This is not the same as oxidation state\textsuperscript{107}, but is a useful approximation as “oxidation state” is not a precisely-defined property on the quantum level. Calculating Bader charges also requires very little additional cost, since the electron density must be computed at every AIMD step. The volume of the electron
density grid assigned to each atom is also computed$^{104}$, and may be useful in determining the many-body polarization effects of solute-solvent interactions.

4.2 Properties that May be Predicted from Classical MD

4.2.1 Viscosity

Viscosity can be computed by using the results of an equilibrium molecular dynamics in tandem with a Green-Kubo (GK) integral of the pressure tensor autocorrelation function$^6$, as shown in equation 4-4.

$$\eta = \frac{1}{k_BVT} \int_0^\infty \langle \sigma_{\alpha\beta}(0)\sigma_{\alpha\beta}(\tau) \rangle d\tau$$

(4-4)

Where $\sigma_{\alpha\beta}$ is a component of the stress tensor. The viscosity is computed for all constituents within the molten salt$^{57}$. The stress tensor autocorrelation portion of equation 4-4 will eventually go to zero, causing a function plateau in the integral, and allowing us to approximate the limit of the integral as $\tau \to \infty$. The Green-Kubo (GK) method relies on correctly identifying this function plateau, which can be ambiguous to identify for shorter simulation times. Therefore, viscosity calculations become reliable as more equilibrated simulation time is used in the analysis$^{50}$. An alternative to using one long trajectory is to use multiple shorter, independent trajectories, and fit the average of the Green-Kubo integrals to a double exponential, minimizing uncertainty and subjectivity,$^{108}$ but this does not reduce the computational time necessary. Therefore, we will not be attempting to predict viscosity values from AIMD but will instead prepare to predict viscosity values once a classical force field has been developed.
4.2.2 Thermal Conductivity

Thermal conductivity is also computed using the Green-Kubo method, but using energy and charge fluctuations rather than the pressure tensor autocorrelation function \(^8, 7^5\). The Green-Kubo method is applied to the coupled heat flux and mass flux, and is thus applied three times in total:

\[
L_{\alpha\alpha} = \frac{v}{3k_B} \int_0^\infty \langle J_\alpha(t)J_\alpha(0) \rangle dt
\]

\[
L_{\alpha\beta} = \frac{v}{3k_B} \int_0^\infty \langle J_\alpha(t)J_\beta(0) \rangle dt
\]

\[
L_{\beta\beta} = \frac{v}{3k_B} \int_0^\infty \langle J_\beta(t)J_\beta(0) \rangle dt
\]

where \(\alpha\) and \(\beta\) are the mass flux and heat flux, respectively. While the mass flux is discretely defined, the microscopic heat flux can be somewhat ambiguous, depending on how one chooses to distribute energies over atoms\(^{109}\). This ambiguity makes it problematic to employ the GK method for systems with non-pairwise interactions, but an alternative method using thermally driven density fluctuations is currently being published by Cheng and Frenkel\(^{109}\). Additionally, if the heat fluxes are calculated using a Green-Kubo method, they must be corrected accordingly to address the Soret effect as outlined by Armstrong and Bresme\(^{110}\). When using the GK method to calculate the thermal flux in systems with large mass or size asymmetries, the Soret effect is observed\(^{110}\). The Soret effect is simply that thermal gradients affect the diffusion rates of different species disproportionately. Uranium, thorium, and other very large solutes are expected to introduce a Soret effect into the salts thermal conductivity, which must be considered\(^{110}\).
4.2.3 Heat Capacity

Heat capacity is computed as the differential of the specific enthalpy, $H$, of the system with respect to temperature at constant pressure$^6, 50, 111$:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$  \hspace{1cm} (4-8)

Where the specific enthalpy is given by:

$$\partial H = \partial U + d(PV)$$  \hspace{1cm} (4-9)

Where $U$ is the internal energy of the system, which is either computed at each step of an MD simulation or fixed, depending on the ensemble used. The pressure and the volume are also either fixed or computed, thus the change in specific enthalpy can be numerically approximated by a large enough body of simulations over a range of temperatures.
5 REQUIREMENTS

The aim of this research is to develop the capabilities to accurately predict the behavior of molten salt mixtures.

When we say we wish to predict a molten salts behavior, we mean three things primarily. First, we want to know the basic thermophysical properties of molten salt mixtures. Second, we want to know what ionic complexes form. Third, we want to predict how adding another trace contaminate will alter these properties and complexes, at least at a basic level.

Achieving these three goals will grant us power in designing the MSR. Besides basic neutronics considerations, knowledge of thermophysical properties and complexations will allow reactor designers to account for supporting features, such as pumping power requirements, heat exchanger sizing, corrosion resistance, and even various separation techniques\(^5\). Furthermore, understanding the general patterns of behavior change will allow us a greater range of safe reactor control.

In order to design safe, effective molten salt reactors, designers must know the thermophysical properties of molten salts and how those properties change as other chemicals such as fuel, fission, and corrosion products are added\(^6\). We do not know much about the properties of the molten salts being considered for MSR design\(^7\). We know even less about how those properties will change as fission products and corroded particles accumulate in the molten salt\(^8\). Many are currently experimenting on molten salt mixtures to determine these properties,
but the number of experiments needed is tremendous. Experimental work is difficult and costly, as material acquisition and safe handling of radioactive chemicals in high temperature molten salts is not simple. If researchers supplement experimental work with computational chemistry, much time, money, and effort may be saved.

It is also important to know where dangerous or valuable species will be found in the system, and in what form. For example, if Molybdenum-99, a rare, radioactive isotope used to make a medical imaging isotope (Tc-99m), is to be harvested from the reactor, we must know where to find it. It could form a fluoride vapor product, or complex with other molybdenum in solution, or freeze onto certain nickel-alloys. We need to know what each such solute will do in solution, and computational approaches allow the direct prediction of solute behavior from quantum mechanics.

While mapping out the entire network of potential solute-solute impacts over all possible concentrations is beyond the scope of this work, a key objective of this research is demonstrating that experimental behavioral predictions can be made from qualitative observations of phenomena in AIMD.

5.1 Salts of Interest

There are several salts of interest for this project. Most are alkali halides. Several major considerations are lithium fluoride-beryllium difluoride (flibe), lithium fluoride-sodium fluoride-potassium fluoride (flinak), magnesium difluoride-sodium fluoride-potassium fluoride (fmgnak), and lithium chloride-potassium chloride (klicl). Some of these salts were tested in the Oak Ridge National Lab Molten Salt Reactor and others are more novel.15
5.2 Solutes of Interest

Solutes of interest that are considered in this work include fuel (uranium), fission and
decay products (molybdenum, cesium, iodide), corrosion products (nickel), and other
contaminants (hydrogen, oxygen, and water).

5.3 Additional Interests

Temperatures investigated in this research are almost exclusively temperatures within the
liquid temperature range of the solution of interest. Concentrations for molten salt solutions are
typically quite dilute for minor components (< 2 mol%), however AIMD simulations are
typically limited to hundreds of atoms, and our CP2K software version integration on the
Brigham Young University Fulton Supercomputer limited computational resources to a single
node. The research presented in this work typically represent systems of 100 atoms or less. The
molar fractions for most salts are typically given as cation fractions, as explained by Fitzhugh et
al\textsuperscript{4}. A fluoride salt system with 100 atoms contains at most 50 cations, which means a single
cation already constitutes 2 mol\% of the total cation population. This then would preclude minor
cOMPONENT interactions with other minor components. Therefore, many studies presented here
have minor component concentrations that are well above what is expected for a true MSR
mixture. However, the chemical interactions of greatest interest are salt-solute interactions and
solute-solute interactions. The inflated concentrations are therefore acceptable and no groveling
for clemency will be forthcoming.
6 METHODOLOGY OF AB INITIO MOLECULAR DYNAMICS OF MOLTEN SALTS

6.1 An Introduction to Molecular Dynamics

Molecular dynamics simulations can predict atoms’ behaviors over time. MD uses a deterministic algorithm to do this. The first step is to create an initial condition. This means you must know what atoms and molecules you want to simulate, how many there are, where they are in your system, and what their initial velocities are. You then choose a time step length. This time step length determines how much discrete time will elapse between each MD iteration. A typical time step is on the order of 1 femtosecond, or $10^{-15}$ seconds. During an MD simulation, the computer calculates the energy potentials and forces acting on each atom in the system, from which an instantaneous acceleration is computed and changes to the instantaneous velocities of each atom are implemented. The system is then allowed to move, and the computing system updates the position of each atom. These new positions are used to calculate the new approximate potentials and forces, and the cycle continues for as many time steps as requested\textsuperscript{112}.

Molecular dynamics simulations originate in the mid-1950s. The method was created by Fermi, Pasta, Ulam, and Tsingou\textsuperscript{113}. Over the next decade, it was shown that the method could be used to simulate perfectly elastic collisions between hard spheres\textsuperscript{114}, simulate radiation damage to solids\textsuperscript{115}, and even simulate liquids\textsuperscript{116}. In that study, Rahman showed that the results
of a simulation could be used to predict system thermophysical properties with surprising accuracy when compared with experimental data\textsuperscript{116}. There are two general classes of MD, classical and \textit{ab initio}.

Classical molecular dynamics (or simply molecular dynamics or MD) relies on specifying a potential energy field model. This model must include parameters to accurately represent the motions and interactions of the atomic constituents of the simulated system. Models considered for molten salt system include the Born-Mayers-Huggins model and variations and derivatives thereof\textsuperscript{6, 50, 58, 62, 66, 88, 89}. Molecular dynamics (MD) is a well-established means of determining thermophysical properties\textsuperscript{50, 98}. The proper selection of a potential model is critical to determining all of the thermodynamic properties of interest to molten salt reactor designers but is outside the scope of this work.

\textbf{6.2 \textit{Ab Initio} Molecular Dynamics}

This work focuses on \textit{ab initio} molecular dynamics simulations of molten salt systems. \textit{Ab initio} molecular dynamics (or first principles molecular dynamics) relies on density functional theory (DFT) to approximate the potential energy effects of electrons in any system more complex than a single nucleus and two electrons.
6.2.1 Density Functional Theory

Density functional theory is an approximation of electronic behavior only. However, it is instrumental in facilitating AIMD. To demonstrate this, we first consider quantum chemistry (it’s a trap!\(^{117}\)) and its culminating theory, the Schrödinger equation:

\[
\begin{align*}
\hat{H} & = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i}^{N} U(r_i, r_j) \\
\psi & = E\psi
\end{align*}
\] (6-1)

The Schrödinger equation yields the energy of a system as an eigenvalue \(E\). The Schrödinger equation requires using operators for electron-electron, electron-nuclei, and nuclei-nuclei interactions, represented by the three terms on the left side of the equation respectively) on the wavefunction \(\psi\) of the system. Thus, any system where the wave function is known can be solved exactly for the energy using the Schrödinger equation. Unfortunately, the wave function of any system more complex than \(\text{H}^+, \text{He}, \text{or Li}^+\) cannot be known exactly, and all molten salt systems require at least 2 nuclei to be of interest.

While the Schrödinger equation is intractable for our purposes, the Kohn-Sham equation works rather neatly. The Schrödinger equation requires a single wavefunction which includes all electrons in the system and is called a many-electron equation. By contrast, the Kohn-Sham equation requires a wavefunction for each electron and then the equations for each electron are combined into a system of equations. The Kohn-Sham equation is given below:

\[
\begin{align*}
\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) & = \epsilon_i \psi_i(r)
\end{align*}
\] (6-2)

The first term of the operator addresses the electron-electron interactions, and the second term accounts for electron-nuclei interactions, as in the Schrödinger equation. The third term, \(V_H\), is the Hartree potential which considers the Coulombic potential of the electron with respect to the total electron density, including self-interaction. The electron density is a three-dimensional
consideration of the probability-weighted charge of the space in a simulation. The fineness of the grid of this space results in the actual electron density of a single discrete point to be quite small for most DFT calculations, however the integral over the entire space results in a charge equal to the discrete charge of the system. The fourth term of the operator, \( V_{XC} \), is the functional derivative of the exchange-correlation energy. Hence the name, [electron] density [exchange correlation] functional theory.

The selection of a proper exchange-correlation (XC) functional is the first step in employing DFT. There are two general classes of XC functionals. Local density approximation (LDA) has its roots in uniform electron gas theory. This is not an ideal fit as molten salts are strongly ionic and polarizable, and the electron density between a cation and an anion is far from uniform. The generalized gradient approximation (GGA) XC functional class has a functional group proposed by Perdew et al. known as the Perdew-Burke-Erzenhof (PBE) XC functional\(^{118}\), which has been found to work well in molten salt systems\(^6, 50, 75, 98, 119\).

Now that we have operators for the 1\(^{st}\), 2\(^{nd}\), and 4\(^{th}\) terms of the Kohn-Sham (KS) equation, we need only to specify the 3\(^{rd}\) term and the single-particle wavefunction and then we can determine the energy; this is done iteratively. First an initial electron density is determined stochastically. This initial electron density is used to solve the KS equation to find the single-particle wavefunctions, \( \psi_i(r) \), for each particle \( i \). We then combine the individual KS equations into a system of equations for all particles in the simulation and calculate the electron density field. If the electron density field is not self-consistent, a new field is generated stochastically, typically with constraints to aid in convergence, and the process is repeated. If the field is self-consistent (within a specified tolerance) to the original stochastic electron density field, the
electron density field is accepted, and the KS solution is used as the potential field in the molecular dynamics motion propagation.

AIMD is functionally similar to MD, and once the forces on each atom are computed, both are deterministic in the molecular dynamics motion propagation scheme, but the AIMD relies on stochastic determination of the electron density field, and so maintains an element of stochasticity that allows for simulations with identical inputs, initial configurations, and parameters to result in distinct molecular dynamics.

Figure 6-1. AIMD simulation of a FLiNaK system containing MoF3 and UF4. The system is mirrored using periodic boundary conditions for illustration purposes. Here yellow is U, light blue is Mo, green is F, purple is Li, dark blue is Na, and pink is K. A brief movie of this or other salt systems illustrated in this work in motion can be obtained by contacting the author. These movies will also bring new meaning to the phrase ordo ab chao.
The DFT approximation to the electron density is a function of the positions of the nuclei, so the DFT iterative process must be repeated at every time step of the simulation. DFT comes at a major computational cost due the complexity of iteratively solving the KS equations at each time step, and is even more restricted in simulation size and duration than the already tiny MD. It is however reasonably accurate for systems which have very few experimentally known parameters, such as molten salts.

6.3 CP2K: An Ab Initio Molecular Dynamics Software Package

The generation of accurate simulations of molten salts is dependent on our selection and implementation of first principles molecular dynamics software and computational basis sets and inputs. We selected the CP2K software for our AIMD simulations\textsuperscript{120}. The program VASP is used by some of our contemporaries\textsuperscript{55,98,119}, however VASP is a private software firm. CP2K was open source, which was key before this research group was sufficiently funded by external sources. CP2K is still developer supported, unlike its predecessor software CPMD, which was also based on Car and Parinello’s foundational work\textsuperscript{112,121}.

CP2K uses the software plug-in QUICKSTEP\textsuperscript{122} in handling the DFT iterations at every time step, and we have already chosen the PBE XC functional\textsuperscript{118}. Thus, our largest remaining burden is selecting electronic basis sets to be used in solving the KS equations. An electronic basis set can include gaussian-type parameters for some or all of the electrons of an element. For small elements like Li, including parameters for all of the electrons is no great burden, but for larger elements such as Mo or U, this can drastically slow the DFT process. Since the electrons closest to the nucleonic core are tightly bound and electronically shielded, they are the least likely to be involved in electron density fluctuations and polarization events. Thus a ‘frozen-
core’ technique is often employed, where only some number of outer-orbital electrons are included in the gaussian basis sets, and the rest of the electrons are treated as part of the core for the solution of the KS system of equations. Pseudopotentials are also employed to account for these core electrons interactions in the self-consistency calculation. The number of core electrons for each element is somewhat flexible in CP2K.

We have elected to include the largest double-zeta-valence basis sets available in the CP2K library\textsuperscript{120}. For smaller elements such as lithium, these include all electrons. For larger elements, these typically include the outer three orbitals at a minimum. This choice is somewhat counterintuitive. The electronic configuration of most species in a molten salt solution is trivial to determine; the salt solvent ions will have filled orbitals. This typically results in stable valence electrons, and inner orbitals that are not chemically active, so to explicitly model those inner electrons may seem a computationally expensive waste. We contend that the polarizability of molten salt ions is a strong function of these inner orbitals, which for large ions tend to reside at comparable distances to valence orbitals. Explicitly modelling these out orbitals allows for more accurate polarization, complexation, and structural formation.

Our simulations typically employ the isobaric-isothermal ensemble, which hold the number of atoms, the pressure, and the temperature constant. This allows us to directly calculate the equilibrium density (See Equation 4-1) and examine the molten salt structure or any complexes formed at a given temperature using only one simulation. Exceptions to using the NpT ensemble will be explicitly discussed.
Figure 6-2. The density of a FLiNaK cell at 940K over time as the energy cutoffs were gradually increased. The final cutoff and relative cutoff values were 2000 Ry and 120 Ry respectively.

Accurate polarization of the electron density requires extremely small energetic tolerances on the DFT self-consistent field iterations, especially in simulations utilizing the NpT ensemble.\textsuperscript{123} This is another nuance of our work which adds to the accuracy of our simulations. Our planewave cutoffs and relative cutoffs are typically much higher than our contemporaries.\textsuperscript{54, 55, 98, 99} As shown in Figure 6-2 and in Figure 9-1, the cell volume of a molten salt simulation is extremely sensitive to minute changes to the system energy, and thus our simulations do not compromise accuracy for using our other design choices.
These are the most peculiar input choices we have found useful in our simulation work. Additional simulation details are found in the methodology subsection of Sections 7, 8, 9, 10, and 11.

6.4 Additional Computational Tools and Software

6.4.1 PACKMOL

PACKMOL is a software for creating initial configurations of atoms\textsuperscript{124}. The number of each ionic species, a minimum radius of exclusion for each species, and the simulation cell size and shape are specified and PACKMOL generates a random initial configuration.

6.4.2 VMD

VMD is predominately a visualization software package, and most figures of atomic configurations found in this work (such as Figure 6-1) are generated using VMD. CP2K employs periodic boundary conditions (PBC) during simulations. If an atom exits the cell wall on one side of the simulation, CP2K creates a mirror image of the atom entering the opposite cell wall. While the atoms are free to traverse in any unrestricted direction, at least one mirror image of every atom is always within the cell boundary. The DFT calculations use the positions of the mirror images to determine the electron density, and then CP2K updates the position of the real atom, and any mirror image within the simulation cell. VMD is excellently equipped to handle wrapping all real atoms into the cell space for ease of visualization and examination. Radial distribution functions (RDFs) are also generated using VMD, which can account for PBC effects. It is against VMD’s programming to impersonate a deity\textsuperscript{117}. 
6.4.3 The Henkleman Group Bader Code

CP2K computes an electron density functional at every step. This can be mapped numerically as an electron density grid. This grid can be ionically partitioned according to the quantum theory of atoms in molecules (QTAIM) criteria of Bader\textsuperscript{105} and using the algorithm and code of the Henkleman group\textsuperscript{104}.

6.4.4 The Fulton Supercomputing Lab

All of this research utilizes the computational resources available at the Brigham Young University Fulton Supercomputing Lab. All the above programs and software are installed on the supercomputer.
7  PURE MOLTEN FLINAK: ITS DENSITY AND STRUCTURE

The capacity to model molten salts using ab initio molecular dynamics to a reasonable level of accuracy was not well established within our department upon the outset of this project. The CP2K software was not well understood by us, and its functionality and our ability to correctly utilize it were not above suspicion. Indeed, the task of drawing conclusions on molten salt behavior that were both broad and specific using tools with which we were unfamiliar seemed much like building a bridge over a tumultuous river.

In 1848, a suspension bridge over a gorge 800-ft wide and 200-ft deep was constructed. The project, thought by many to be impossible, was achieved after a young boy flew his kite across the gorge, and his kite string was used to pull thicker and thicker cords and wires across. In like manner, this project used a single, simple benchmarking project to validate and verify our methodology. While less exciting than flying a kite across the Niagara, we successfully examined the structure of a molten salt using a combination of neutron diffraction techniques and our ab initio molecular dynamics simulations. FLiNaK, a salt of interest to the development of molten salt nuclear applications, was chosen for this study. One reason for this choice is the relative simplicity of the ionic interactions of FLiNaK, which contains only monovalent ions, as opposed to the salts FLiBe or FMgNaK, which contain divalent cations. Divalent cations have profound impacts on local salt structures and also tend
to coordinate tetrahedrally instead of octahedrally, as will be demonstrated in our subsequent discussion, which is taken from our publication1.

The structure of the molten salt (LiF)0.465(NaF)0.115(KF)0.42, or FLiNaK, a potential coolant for molten salt nuclear reactors, has been studied by ab initio molecular dynamics simulations and neutron total scattering experiments. We find that the salt retains well-defined short-range structural correlations out to approximately 9 Å at typical reactor operating temperatures. The experimentally determined pair distribution function can be described with quantitative accuracy by the molecular dynamics simulations. These results indicate that the essential ionic interactions are properly captured by the simulations, providing a launching point for future studies of FLiNaK and other molten salts for nuclear reactor applications.

Molten salt reactors (MSRs) are a promising nuclear reactor concept in which fuel and/or fertile material are dissolved directly into a halide salt coolant. This has significant benefits over traditional light water reactors (LWRs) that are in operation today, including the capability of producing medical radioisotopes and electricity simultaneously in large amounts126 and the possibility of reactor designs that prevent proliferation of weaponizable material, eliminate the risk of meltdown events, and avoid producing long-lived transuranic nuclear waste127, 128.

The feasibility of molten salt thorium-fueled reactors and their potential for fuel breeding was validated through the Molten Salt Reactor Experiment (MSRE), which operated from 1965 to 1969 at Oak Ridge National Laboratory129. However, licensing commercial MSRs requires the validation of several additional fundamental chemistry concepts that were not accomplished in the MSRE, including chemical separation techniques, isotope extraction techniques, corrosion potential, ion-ion interaction potentials and subsequent impacts on thermophysical properties of the coolant, and the structure and speciation of the fission products in the salt. In addition, the
MSRE project made no efforts to explore medical isotope production\textsuperscript{130}. Little work was done on MSRs for many years following the MSRE.

Growing interest in MSR technology in recent years has led to renewed research efforts on this topic\textsuperscript{128, 131}. One of the most urgent issues is to establish the structure and speciation in the molten salt coolant with and without fission products\textsuperscript{132}, as this information plays a key role in developing transport and thermodynamic models. This is especially challenging because over 50 elements (fission products, fuel, and transuranic elements) are dissolved in the coolant at any given moment\textsuperscript{133}. The first step toward this ambitious goal is to determine the structure of pure coolant salts without any fuel or fission products. Gaining insight into the speciation and complexation of the ions in the melt will provide a basis for understanding numerous basic properties such as viscosity, thermal conductivity, activity coefficients, and more, supporting the goal of developing reliable theoretical simulation models used for optimizing MSR systems.

In this work, we present pair distribution function (PDF) analysis of neutron total scattering data collected on the salt known as FLiNaK, a eutectic mixture of LiF, NaF, and KF that has been proposed as a promising salt coolant for use in MSR applications. PDF is an excellent tool for quantitatively probing the local structure of liquids, including molten salts\textsuperscript{134-136}. The PDF measurements reported here provide a rare opportunity to probe the structure of FLiNaK directly, marking an important development in the field. Further, ab initio molecular dynamics (AIMD) simulations of FLiNaK were also performed, with the resulting structure predictions being compared directly to the PDF data. We show that the AIMD structures reproduce the measured PDF data with quantitative accuracy. These results provide detailed information about the local ionic correlations in FLiNaK for the first time and demonstrate that the AIMD framework utilized here is reliable. A pure, isolated sample of FLiNaK was produced.
for the neutron scattering experiment as follows. Individual components of LiF, NaF, and KF in a 46.5-11.5-42 mol % composition were dried in a vacuum oven for 6 hours at 300°C. These were then passed into an anaerobic, anhydrous argon-filled glovebox where they were combined and melted at 600°C in a nickel crucible. This melt was then subjected to argon sparging for 48 hours at a flow rate of 1 L/min to remove residual moisture and particulates. The molten salt mixture was then electrolyzed at a voltage of 1.5 V for 72 hours to remove soluble impurities. Lastly, the melt was filtered through an alumina filter with an average pore size of 2 mm to remove additional solid impurities and then allowed to cool and solidify.

Neutron total scattering experiments were performed on the NOMAD beamline at the Spallation Neutron Source using a vacuum furnace to access temperatures between 25°C and 1000°C. A 1.63 g sample of FLiNaK was crushed into a powder in an argon glove box near the beamline, loaded into a vanadium sample can, and placed in the beamline furnace chamber, which was subsequently evacuated. The closed sample can was in air for less than 30 s during this process. The total scattering structure function \( S(Q) \) was obtained from the neutron time-of-flight data following standard data reduction protocols, including absolute normalization using a vanadium rod for reference. Scattering patterns obtained at temperatures below and above the melting point (454°C) were collected for a total integrated proton charge of 4 C and 12 C, respectively. The suppression of the scattered intensity at low momentum transfer \( Q \) due to the large neutron absorption cross section of natural Li (arising from the \(^6\)Li isotope) was corrected empirically using a hydrogen-type Placzek correction fitted to the scattering pattern in the range of \( 1 < Q < 20 \ \text{Å}^{-1} \).
The experimental pair distribution function (PDF) \(g(r)\) was generated for each total scattering pattern according to the relationship \(^{138}\)

\[
g(r) - 1 = \frac{1}{2\pi^2 r_0} \int_0^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ
\]

(7-1)

where \(\rho_0\) is the number of atoms per unit volume and \(Q_{max} = 15\ \text{Å}^{-1}\), estimated to be the largest value of \(Q\) for which meaningful scattering signal in the molten state remained larger than statistical noise in the data. For scattering patterns collected at temperatures below the melting point, the reduced PDF \(G(r) = 4\pi r_0 = [g(r) - 1]\) was also generated with \(Q_{max} = 20\ \text{Å}^{-1}\). Fits to \(G(r)\) were performed using the program PDFgui\(^{139}\). AIMD simulations based on density functional theory (DFT) were performed using the CP2K software package\(^{120}\). Calculations utilized the Perdew-Burke-Ernzhof (PBE) exchange-correlation functional\(^{118}\), a form of general gradient approximation (GGA).

Figure 7-1. Density of FLiNaK determined from the AIMD simulations in the present work (blue circles, with the solid turquoise line showing a linear fit) compared to experimentally estimated values from An et al, Chrenkova et al., and Powers et al.\(^{5,140,141}\).
The Gaussian and plane waves method (GPW) was used, in which wave functions are represented by atom-centered Gaussian orbitals and the electron density is represented by planewaves\(^{122}\). Within this framework, all atoms were modeled using DZVP-MOLOPT-SRGTH basis sets\(^{90}\) with core electrons treated with Goedecker-Teter-Hutter pseudopotentials\(^{90,120}\). Simulations were performed in the NPT ensemble, with pressure held at atmospheric pressure through the method of Martyna et al.\(^{142}\) and temperature held constant through the Nose-Hoover thermostat\(^{143}\). All simulations had a time step of 0.5 fs. The simulation cell was considered equilibrated if the average density over a period of 5 ps (10,000 steps) was within 2% of the average density of the next 5 ps. The NPT ensemble is sensitive to relatively small errors in calculated energy, and so high energy cutoffs were required for predicted densities to converge: 2000 Ry for the plane-wave energy cutoff, and 120 Ry for the relative cutoff, which in the GPW method corresponds to the planewave cutoff of a reference grid on which Gaussians are mapped. The predicted densities were remarkably close to experiment. Figure 7-1. Density of FLiNaK determined from the AIMD simulations in the present work (blue circles, with the solid turquoise line showing a linear fit) compared to experimentally estimated values from An et al, Chrenkova et al., and Powers et al.\(^3,140,141\). Figure 7-1 shows density versus temperature determined from MD simulations (each data point representing an equilibrated simulation cell containing 50 FLiNaK atoms) and compared to experimental results from the literature\(^3,140,141\). An additional simulation using a cell with 100 atoms of FLiNaK at 667 °C yielded an equilibrated density within 0.2% of the expected value at that temperature from experimental correlation reported by Chrenkova et al.\(^3\) (well within the 2% margin of error of that correlation). This simulation cell was used to calculate radial distribution functions for comparison with neutron scattering data. We note that including corrections for Van der Waals dispersion in the simulations resulted in a
predicted density that differed from the experimental correlation by 4%. It is known that the
efficacy of Van der Waals dispersion corrections is dependent on the details of a given
simulation, improving the accuracy in some cases but not in others (including this study)\textsuperscript{1,98}.
Determining a priori which combination of simulation methods is most legitimate is difficult,
and comparison to experiment remains the best way of testing the validity of any particular set of
methods. As such, dispersion corrections were omitted from all simulations used in this study.

![Figure 7-2. Total scattering structure function S(Q) for molten FLiNaK at 467 °C and 980 °C, offset vertically for clarity.](image)

We now present the results of our combined neutron total scattering and AIMD studies.
In Figure 7-2, we display the total scattering structure function S(Q) for molten FLiNaK at 467
°C and 980 °C (the highest temperature attained during the experiment). The patterns are typical
for liquids. The diffuse features in $S(Q)$ persisting out to approximately 12–15 Å$^{-1}$ arise from well-defined short-range ionic correlations. The features in the scattering pattern become increasingly broad and weak as the temperature increases from 467 °C to 980 °C, indicating that the short-range correlations become less well-defined at higher temperatures. At lower temperature in the solid state$^1$, sharp Bragg peaks are present, indicating crystalline order. Fits to the reduced PDF $G(r)$ for solid FLiNaK assuming a phase-separated mixture of the three binary salts LiF, NaF, and KF are significantly better than fits assuming a uniform distribution of the cations, indicating that solid FLiNaK has significant inhomogeneity.

A more intuitive view of the structure of FLiNaK can be gained by examining the real-space PDF patterns. Peaks in the PDF correspond to ion-ion pairs separated by the value of $r$ at which the peak is found, with the sign and size of the peak determined by the number of ion pairs separated by that distance and the product of the neutron scattering lengths of the corresponding ions.

To examine the evolution of the structure through the melting point, we plot the PDF $g(r)$ at several temperatures in Figure 7-3. At 25 °C, well-defined features in the PDF persist over the entire displayed range, as expected for the long-range order in the solid state.

The first peak in $g(r)$ at 25 °C is negative and centered around $r = 2.0$ Å, corresponding to the first nearest neighbor Li-F peak. Li has a negative scattering length and F has a positive scattering length, so all Li-F peaks are negative. The nearest-neighbor (NN) Na-F and K-F peaks are both positive due to the positive scattering lengths of Na and K, but they are less clearly
Figure 7-3. The PDF $g(r)$ of FLiNaK at various temperatures below and above the melting point. The solid-liquid transition is clearly seen through the loss of well-defined features at high $r$ above the melting point.

visible in the pattern. From fits to the reduced PDF $G(r)$ at 25 °C (not shown), the NN Na-F peak is expected to occur at 2.32 Å. There is indeed a small feature in $g(r)$ at this position, but the low concentration of NaF greatly reduces its magnitude. The NN K-F peak is centered around 2.67 Å, overlapping significantly with the first Li-Li and F-F peaks at 2.85 Å from the LiF component. As the temperature is raised from 25 °C to 433 °C, the peaks in the PDF patterns become increasingly broad due to thermal vibration, but well-defined features persist over the full $r$ range.

The PDF patterns change dramatically in the molten state, as seen in Figure 7-3 for the data collected at 467 °C and above. A strong negative peak is still clearly visible at low $r$, indicating that the Li-F nearest neighbors are still well correlated. Interestingly, this first negative peak shifts from 2.0 Å in the solid state to 1.8 Å in the molten state, demonstrating that the
strong attraction between Li$^+$ and F$^-$ results in a shorter average ionic bond in the molten state than in the solid state. A similar effect has been observed in other molten salts such as NaCl$^{144}$. On the basis of the AIMD simulations to be described later, we associate this shortening of the Li-F bond to a reduction of the coordination number from 6 in the solid state to 4 in the molten state. The nearest-neighbor Na-F and K-F peaks are included in the broad positive peak observed between approximately 2 Å and 3.5 Å, along with contributions from various other ion pairs. Two additional weak and broad peaks centered around 5.5 Å and 8 Å can also be observed in Figure 7-3 for the data collected at 467 °C, 500 °C, and 600 °C, but beyond approximately 9 Å, any remaining features in the PDF are comparable to the noise level. At 980 °C, the broad peak centered on 8 Å is not clearly resolvable, indicating that the non-random correlations on this length scale have been significantly weakened with increasing temperature.

We now turn to the AIMD simulations to extract more detailed information about the local structure and interactions in molten FLiNaK. After a given simulation converges, the ionic configurations can be averaged over a suitable period of time (40 ps in this case) and used to calculate the partial PDFs for each distinct type of ion-ion pair. These partial PDFs can then be summed together using the concentrations and scattering lengths as weights to generate the total PDF for comparison with the experimental PDF.

The calculated PDF determined from the AIMD simulation of FLiNaK at 667 °C, a typical nuclear reactor operating temperature, is compared to the experimental PDF measured at 600 °C in Figure 7-4(a).

The experimental data and calculated PDF are shown as the black symbols and red curve, respectively. As seen in the figure, the calculated PDF provides an excellent match to the data over the first 8.35 Å, confirming that the AIMD simulations yield a realistic model of the
structure of molten FLiNaK. The simulation box size prevented us from calculating the PDF over larger distances, but this is not a significant limitation, since any observable features beyond ~9 Å are severely limited. In Figure 7-4(b), we show the partial PDFs $g_{\alpha\beta}$ determined from the simulations, corresponding to the correlations between each distinct type of ion-ion pair. Note that the partial PDFs have not been weighted by concentration or scattering length. The three most prominent peaks are Li-F, Na-F, and K-F, with maxima at approximately 1.84 Å, 2.20 Å, and 2.60 Å, respectively. These peaks are all at slightly shorter distances than the nearest-neighbor cation-anion bond lengths in solid FLiNaK, with the Li-F peak being shifted to shorter $r$ most significantly. This is consistent with the observed shift in the negative Li-F peak across the melting point in Figure 7-3, demonstrating that the simulations accurately capture this effect. Subsequent partial PDFs are significantly broader, indicating that the corresponding correlations are more widely distributed in real space.

Nearest-neighbor (NN) peak distances and coordination numbers extracted from the AIMD simulations are shown for the most important ion pairs in Table 7-1, along with the results from an earlier x-ray scattering experiment\textsuperscript{97}.

The NN peak distances are in excellent quantitative agreement between the two studies. On the other hand, the coordination numbers show the same qualitative trend, but significant quantitative discrepancies exist. We note that the earlier x-ray study had much more limited sensitivity to the light elements in FLiNaK than the present neutron study, and that their method of determining the coordination numbers considered only the NN correlations of
Figure 7-4. (a) Observed PDF and calculated PDF determined from AIMD simulations of FLiNaK. The excellent agreement demonstrates that the simulations provide an accurate picture of the structure of molten FLiNaK. (b) The partial PDFs $g_{\alpha\beta}$ extracted from the AIMD simulations, displayed over the first 5 Å. Note that these partial PDFs have not been weighted by the concentrations or scattering lengths of the ions.
Table 7-1. Nearest-neighbor (NN) peak distances and coordination numbers for various ion pairs determined from the AIMD simulations and an earlier x-ray scattering study98.

<table>
<thead>
<tr>
<th></th>
<th>NN peak (Å)</th>
<th>Coordination Number</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AIMD</td>
<td>EXP98</td>
<td>AIMD</td>
<td>EXP98</td>
</tr>
<tr>
<td>Li⁺–F⁻</td>
<td>1.84</td>
<td>1.83</td>
<td>4.00</td>
<td>3.3</td>
</tr>
<tr>
<td>Na⁺–F⁻</td>
<td>2.20</td>
<td>2.18</td>
<td>5.42</td>
<td>3.8</td>
</tr>
<tr>
<td>K⁺–F⁻</td>
<td>2.60</td>
<td>2.59</td>
<td>7.12</td>
<td>4.0</td>
</tr>
<tr>
<td>F⁻–F⁻</td>
<td>3.10</td>
<td>3.05</td>
<td>11.2</td>
<td>8.9</td>
</tr>
</tbody>
</table>

the three unlike-ion pairs and F⁻–F⁻ and K⁺–K⁺, ignoring all others. For these reasons, we consider the coordination numbers extracted from the present AIMD simulations to be more reliable. The results presented here provide a crucial contact point between theory and experiment. The success of the AIMD simulations in describing the experimental PDF data demonstrates that we have an appropriate model for FLiNaK, which until now has been lacking a sound experimental basis. Detailed structural information from the simulations can therefore be extracted and used confidently for further theoretical and experimental work. Specifically, this work sets the stage for future studies that use the AIMD-predicted structure to explore solution chemistry and the solution complexes that form around fission products, providing direct insight into the behavior of the system under operating conditions in a molten salt reactor. Now witness the fire-power of this fully armed and operational battle station117.
Having demonstrated the accuracy of our simulation methodology with the well-known and highly studied salt FLiNaK, we now branch out to a relatively unknown fluoride salt, FMgNaK, to explore its density and structure. We draw now from a work that is under publication review at the time of this writing.

8.1 Introduction to the Characterization of the Molten Salt FMgNaK

The selection of a salt species for use in a molten salt reactor MSR is a key part of any MSR design. However, many salts have sparse or no thermophysical property data sets, especially those with higher melting points. One such salt is the eutectic mixture of (NaF)\textsubscript{0.345}(KF)\textsubscript{0.59}(MgF\textsubscript{2})\textsubscript{0.065}, or FMgNaK, and is explored here through ab initio molecular dynamics (AIMD) simulation (1023-1273 K) as well as experimental measurement of the liquid density using the Archimedean method (973-1223 K). After validating the AIMD simulation density of FMgNaK with the experimentally determined density, we explore other thermophysical properties of FMgNaK such as the coefficient of thermal expansion and the coefficients of self-diffusion. We also examine structural properties, such as ionic coordination and Mg-F-Mg chaining in the salt network, as well as electronic properties such as the partial electronic charges of the ions in solution. While Mg-F-Mg chaining is observed, the low
concentration of Mg inhibits chaining on the scale that is observed in (LiF)_{0.67}(BeF_2)_{0.33}, or FLiBe. This work meaningfully expands the property data set for FMgNaK and provides insights on salt structure. The close agreement between experimentally and computationally determined density demonstrate the contemporary feasibility of higher operating temperatures in MSRs and also adds veracity to the accuracy of AIMD simulation when applied to the modelling of molten fluoride salts.

While several eutectic mixtures of halide salts have been considered as coolants for molten salt reactors (MSRs)\textsuperscript{27}, one salt that has received relatively little attention is (NaF)_{0.345}(KF)_{0.59}(MgF_2)_{0.065}, or (FMgNaK). FMgNaK poses an economical alternative to the expensive purification process of FLiBe\textsuperscript{145}, or (LiF)_{0.67}(BeF_2)_{0.33}, which is the most common\textsuperscript{27} salt used in MSR designs. FMgNaK has comparable heat capacity, thermal conductivity, and neutron absorption\textsuperscript{146} without intense $^7$Li-enrichment, which added $10,000/kg to the cost of FLiBe in 2012\textsuperscript{145}. Indeed, $^7$Li-enrichment is needed for many molten salt alternatives (FLiBe, FLiNaK, LiF, KLiCl) as natural lithium produces tritium, which permeates through the reactor, severely harming both the reactor and the environment\textsuperscript{147, 148}. $^6$Li also has a large neutron absorption cross-section, making it a significant neutron poison\textsuperscript{149}. FMgNaK, however, does not require any lithium, making the salt less expensive, less poisonous to neutronics, and safer to produce in large quantities. Handling beryllium is also very dangerous. Acute skin exposure or inhalation can quickly cause chemical pneumonia, lung diseases, and even lung cancer, among many other ailments\textsuperscript{150}. On the other hand, while personal protective equipment is still required to handle FMgNaK, none of its components are highly toxic and none are suspected carcinogens\textsuperscript{151-154}. Additionally, in a neutronic analysis of thermal diffusion length and fermi
age, the components of FMgNaK rival the components of FLiBe, having excellent neutronic properties\textsuperscript{146}.

Despite these advantages, FMgNaK has not traditionally been considered for MSR designs as salt temperatures for early reactors only reached a maximum of between 720-750 °C\textsuperscript{30}: just barely above FMgNaK’s eutectic melting point of 685 °C\textsuperscript{155}. However, improvements in material science and fabrication techniques enable modern reactors to reach much higher temperatures, bringing the salt back into the limelight\textsuperscript{156}. Still, because FMgNaK has been overlooked for so long, its properties are even less well-characterized than other salts, with no entry in even large, inclusive databases of molten salt properties\textsuperscript{157}.

This paper uses ab initio molecular dynamics (AIMD) simulations to predict several thermophysical properties of molten FMgNaK, as well as characterizing its structure. FMgNaK density was also experimentally measured using the Archimedean method modified to account for surface tension, which we expect to significantly improve accuracy over other methods. These experimental measurements will be used to validate our AIMD simulations.

AIMD has been used to study several molten fluoride salts including (LiF$_{0.465}$(NaF)$_{0.115}$(KF)$_{0.42}$ (FLiNaK), and FLiBe\textsuperscript{1, 50, 55, 73-75, 92, 119, 158}. AIMD simulations of FLiNaK from our own lab were found to compare favorably to the results of neutron scattering experiments\textsuperscript{1}. AIMD also has the advantage of not requiring an interatomic potential model, unlike classical molecular dynamics, which is helpful for a little-studied material like FMgNaK which does not have established potentials.
8.2 Methodology for the Characterization of FMgNaK

8.2.1 Simulation Methods

We created a simulation cell for each of 20 AIMD production runs. Each cell contains 95 atoms with a eutectic composition of NaF-KF-MgF$_2$ (49 F atoms, 3 Mg atoms, 16 Na atoms, and 27 K atoms). Initial configurations of atoms were generated at random using the Packmol software package\textsuperscript{124, 159}.

We performed AIMD simulations using the CP2K software\textsuperscript{120, 160}. These simulations were based on density functional theory (DFT), and utilized the Perdew-Burke-Ernzerhof (PBE) exchange-correlational functional\textsuperscript{118}, which is a form of the generalized gradient approximation (GGA). We employed the Gaussian and plane waves method (GPW) to approximate the wavefunctions and electron density\textsuperscript{122, 161, 162}. All atoms were modelled using DZVP-MOLOPT-SR-GTH basis sets\textsuperscript{90, 163}, and all core electrons were treated with GTH pseudopotentials\textsuperscript{90, 120, 164, 165}. A detailed explanation of our AIMD methodology is also given by Frandsen et al., and was found to accurately predict molten salt structure of FLiNaK compared to neutron scattering data\textsuperscript{1}. The main difference between methodology described in that publication and the work described here is the values of the GPW cutoffs used: this work uses 2500 Ry for the plane-wave energy cutoff, and 200 Ry for the relative cutoff (the plane-wave cutoff of the reference grid upon which the gaussians are mapped).

The temperature was controlled using the canonical sampling through velocity rescaling\textsuperscript{166} (CSVR) thermostat, which is purported to be more ergodic than the Nosé-Hoover thermostat\textsuperscript{166}. The system barostat also employed canonical sampling through velocity rescaling. We simulated FMgNaK over the temperature range 750-1000 °C. We used the NPT ensemble with an external pressure of 1 atm and a timestep of 0.5 fs. We allowed the simulations to
equilibrate for 20 ps and obtained our equilibrium properties by averaging the following 20 ps of the simulation, a technique successfully employed by Caro et al\textsuperscript{167}.

The density of a simulated molten salt is quite sensitive to the interaction energies of a system\textsuperscript{50, 98} and so an accurate density prediction is a reasonably good indication that simulated energies are adequate to describe the behavior of a molten salt system. Density is calculated straightforwardly from the NPT ensemble, taking:

\[
\rho = \frac{m}{V(T)}
\]  

(8-1)

where \( m \) is the total mass of all particles in a cell and \( V(T) \) is the equilibrium volume as a function of temperature. Density of molten salts at this temperature range has traditionally been fit to a simple linear regression for a wide range of fluoride salts\textsuperscript{15, 18, 168, 169}. A D-optimal design of experiment for a simple linear regression mandates that the variance be minimized for the two extreme points of the range being investigated. In our case this means that the highest and lowest temperatures simulated carry more information about the density than any other two temperatures within the range simulated. Our 20 simulations were thus weighted towards either end of the temperature range of interest.

To verify that the liquid density is indeed a linear function of temperature over the range investigated, and to allow for regression of other properties of interest, several intermediate temperatures were also simulated. The number of simulation cells at each temperature simulated is given in Table 8.1.
Table 8-1. A list of the simulated temperatures and the number of simulations conducted at each temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Quantity</th>
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<tbody>
<tr>
<td>750</td>
<td>6</td>
</tr>
<tr>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>850</td>
<td>2</td>
</tr>
<tr>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>950</td>
<td>2</td>
</tr>
<tr>
<td>1000</td>
<td>6</td>
</tr>
</tbody>
</table>

We ensured simulations were equilibrated by testing if the average density over a period of 5 ps (10,000 steps) was within 2% of the average density of the subsequent 5 ps. This definition of equilibration has been successfully used in AIMD simulations by Frandsen et al.\textsuperscript{1}

From the temperature dependency of our density measurements, we calculated the coefficient of thermal expansion (CTE; $\alpha$) using Equation 8-2.

$$
\alpha \equiv \frac{1}{V} \left( \frac{dV}{dT} \right)_p = -\frac{1}{\rho} \left( \frac{d\rho}{dT} \right)_p \tag{8-2}
$$

where $T$ is the temperature, $\rho$ is the density, and $V$ is the volume. This technique has been successfully used to calculate CTE in literature\textsuperscript{55} and is an accurate method of determining thermal expansion in liquids. Our density simulations are also directly compared to experimental measurements, making properties directly derived from density similarly verifiable.

Radial distribution functions (RDFs) contain valuable information about the structure of a material, especially within the first peak. The normalized height of the first peaks in the RDFs correspond to the relative strength of the interaction between the ions, and the x-axis coordinate value of each first peak indicates the most probable radial distance between an ion of species $a$ and another ion of species $b$ within its solvation shell. The normalized integral of the RDF up to
the terminus of the first peak yields the average coordination number of species \(b\) with respect to species \(a\).

RDFs were generated from the CP2K-generated trajectory files using the Visual Molecular Dynamics (VMD) software package\(^{170}\) and these RDFs incorporate periodic boundary conditions (PBC). RDFs are used to determine the structure and potential speciation of the ions in FMgNaK.

We use the velocities of the ions at every timestep to calculate the self-diffusion coefficient \(D_\alpha\) of component \(\alpha\) in any system using the Green-Kubo formula shown below which relates the self-diffusion coefficient of component \(\alpha\) to the velocity autocorrelation function\(^{171}\).

\[
D_\alpha = \frac{1}{3 N_\alpha} \sum_{k=1}^{N_\alpha} \int_0^\infty \langle \vec{u}_k(t) \cdot \vec{u}_k(0) \rangle dt
\] (8-3)

where \(N_\alpha\) represents the number of ions of component \(\alpha\), \(\vec{u}_k(t)\) represents the vector velocity for ion \(k\) at time \(t\), and \(\vec{u}_k(0)\) represents the initial vector velocity of ion \(k\). Diffusion coefficients were calculated using simulation data generated after the 20 ps of equilibration. Diffusion events are difficult to capture in the short timescales of AIMD, lending to large variance in AIMD diffusion values\(^{172}\). To mitigate this effect, we used data from every 200 timesteps (100 fs) to calculate diffusive properties as detailed by He et al.\(^{172}\)

We estimated partial atomic charges using Bader’s atoms in molecules (AIM) electron density partitioning scheme\(^{105}\) as implemented by the Henkelman group\(^{104}\). In such a Bader charge analysis, the atomic charge distributions are integrated over the Bader volumes, whose boundaries are defined by the zero-flux surfaces in the total cell charge distribution\(^{105}\). After our simulations completed their 20 ps of equilibration, Bader analyses were performed on frames taken every 25 fs for a total of 3 ps. This analysis was performed on and averaged over each of our equilibrated simulations. We averaged the Bader charges for each ionic species over the
equilibrated simulations and across our temperature range, a temperature independent assumption made on similar fluoride salts\textsuperscript{55}.

Bader charges are an approximation of atomic contributions to electron charge density\textsuperscript{104, 105}. The charge distribution at a point \( r \) within a unit cell can be approximated by:

\[
\rho = N \int \psi^*(x; X)\psi(x; X) \, d\tau'
\]

where \( N \) is the number of electrons, \( \tau' \) denotes the spin coordinates of all the electrons and the Cartesian coordinates of all the electrons but one, and \( \psi(x; X) \) is a solution to the stationary-state Schrödinger’s equation for a fixed arrangement of the nuclei\textsuperscript{105}. The charge distribution densities are assigned to a nuclei using a steepest-ascent method of a grid representation of the electron density\textsuperscript{104}. The summation of the discrete charges of all points in a volume assigned to a nucleus yields the Bader charge of an ion. This charge is not necessarily an integer value\textsuperscript{106}, and classical molecular dynamics models used to simulate molten salts will benefit from a more accurate ionic charge value.

8.2.2 Experimental Methods

To prepare FMgNaK salt, we first purchased the component salts KF, NaF, and MgF\(_2\) from Sigma Aldrich at 99.99% purity. We then dried each salt in a dry box at 500 \( ^\circ \text{C} \) for twenty-four hours, after which we weighed and mixed each salt in their respective molar ratios, \((\text{NaF})_{0.345}(\text{KF})_{0.59}(\text{MgF}_2)_{0.065}\). We then melted and mixed the solid powder mixture at 700 \( ^\circ \text{C} \).

We built a density measurement device that operates on the Archimedean method, which was chosen for its robust and relatively simple design\textsuperscript{173}. Sandia National Laboratory used the Archimedean method to measure the density of several nitrate salts and documented their experimental setup in great detail\textsuperscript{174}. A bob of known volume was submersed in a liquid, and the
resulting buoyancy force was used to calculate the density. The buoyancy force was the difference between the force on the stationary bob in air/argon and the force on the stationary bob submerged in the liquid of unknown density.

Due to the highly oxidative nature of fluoride salts, nickel was chosen as the bob material because of its low reactivity\textsuperscript{175}. All materials directly in contact with the molten salt are made of pure nickel except the Type-K thermocouple sheath, which is made of a resistant nickel alloy used in literature to measure molten fluoride salts\textsuperscript{176}.

![Diagram]

Figure 8-1: BYU Molten Salt Laboratory Archimedean method density apparatus diagram. a – Mettler Toledo analytical scale with hook for mass underneath: model ML503T or MS303TS, b – stainless steel heavy duty scissor lift, c – Paragon SC-2 Pro Furnace with Orton SntryXpress 5.0 Controller, d – Omega Industry Type-K thermocouple, e – nickel wire, f – nickel bob.

The volume of the bob/probe (f) is first determined by performing this experiment with 18-ohm resistant water at room temperature, solving for probe volume using the known density of water. A correction for thermal expansion of the nickel probe must be included for accurate
measurement as there is a large temperature difference between probe volume determination at room temperature and salt measurements and between salt measurements (roughly 25-950 °C)\textsuperscript{174}. The tension force is measured by the scale (a) at a given temperature (using the thermocouple (d)). From the tension force difference between the weight of the bob in air (argon was used in our glove box) and the weight of the bob in salt the buoyancy force is calculated. From the buoyancy force, the density is determined using Equation 8-5.

\[
\rho = \frac{F_b}{g \cdot V(T)}
\]  

(8-5)

where \(\rho\) is the density of the liquid, \(F_b\) is the buoyancy force, \(g\) is the gravitational constant, and \(V(T)\) is the volume of displaced salt as a function of temperature. The probe used in this experiment was 99.99% pure nickel and the volume of the bob was adjusted for thermal expansion of the material using the empirical expression supplied by Abdullaev et al.\textsuperscript{177}. The buoyancy force as measured by the scale was corrected by including the surface tension of the salt and the buoyancy in air/argon. The surface tension of fluoride salts is relatively unknown, but placeholder values of 200 \(\frac{\text{dyn}}{\text{cm}}\) have been successfully used to yield correct density values in literature\textsuperscript{168}. We used this placeholder value for the surface tension of FMgNaK. The corrected form of the buoyancy force is as follows:

\[
\rho_{salt} = \frac{F_{T_0} + \frac{M_{Ar}P}{RT_0} g V_{\text{probe}}(T_0) + 4\gamma \pi D_{wire} - F_{T_1}}{g V_{\text{probe}}(T_1)}
\]  

(8-6)

where the \(F_{T_0}\) is the measured tension force of the probe surrounded by air/argon, \(M_{Ar}\) is the molar mass of the supporting fluid (air/argon) prior to submersion in salt, \(P\) and \(T_0\) are the pressure and temperature of the supporting fluid respectively, \(V_{\text{probe}}(T)\) is the volume of the
probe at a given temperature, $\gamma$ is the interfacial tension between the supporting fluid and salt, $D_{\text{wire}}$ is the diameter of the wire under tension supporting the probe, and $F_{T_1}$ is the measured tension force at $T_1$ (the temperature of the molten salt) when the probe is immersed in the salt solution. The surface tension force can be either attractive or repulsive, but for the salt solutions used in these experiments upwards wicking of the salt onto the bob was consistently observed, thus the surface tension force is very likely attractive. Hence the sign on the surface tension force is positive in Eq. (8-6). Although the formula for surface tension is $2\gamma \pi D$, the wire used in our experiment passed through the interface of the solution twice, doubling the effect of surface tension. The surface tension component of Equation (8-6) is doubled as a result. Calibration of the density apparatus can be found in Appendix A of this forthcoming work but is not included here.

FMgNaK density was measured at a set of temperatures, $T= [700, 750, 800, 900, \text{ and } 950 ^{\circ}\text{C}]$. The salt was measured at each temperature in the set following a randomly selected order. The entire measurement process was repeated three times on the same salt sample using a new bob-wire and initial condition measurements on each set.

The Archimedean method has inherent error. Salt vapors can deposit on the wire increasing the tension force on the wire when the bob is submerged in the salt. This creates a bias for the measured density to be lower than the true density. The effect of salt vapor deposition is a function of time and salt temperature, increasing with both variables. Randomizing the order of measurement in each temperature removes this effect as a confounding variable when analyzing the density on temperature dependance\textsuperscript{178}. The wire in both the nitrate salt calibration and fluoride salt test showed no visible salt deposition. Invisible salt deposition could only amount to
a maximum of 10 mg in the in-salt scale measurement which amounts to a maximum of 0.03% error in density.

The surface tension of the salt is unknown and a stand-in value of \(200 \frac{dyn}{cm}\) was used for the density calculation. The error associated with this simplification can be estimated from other similar salt compounds. The surface tension measured for the close-in-composition-mixture \(\text{NaF}_{0.4\text{mol\%}}-\text{KF}_{0.6\text{mol\%}}\) ranges from about 152 to 172 \(\frac{dyn}{cm}\) over the temperature range from 625-875 \(^\circ\text{C}\). A difference of 50 \(\frac{dyn}{cm}\) equates to about 0.09% error in density measurement.

The presence of water in the salt leads to corrosion products of the container material, shifting the mixture concentration and altering the measured density from the true density\(^{179}\). An ICP semiquantitative analysis allows for us to measure the degree of corrosion and mixture contamination present due to container corrosion. The ICP semiquantitative analysis gives an order of magnitude concentration estimate of corrosion metals. The Ni, Cr, and Fe concentrations in the salt is two orders of magnitude lower than the main metal constituents. From this information, we can make an estimate of the potential effect of these contaminants on the density measurement using molar volume additivity model. Estimating the molar volumes of \(\text{NiF}_2\), \(\text{CrF}_2\), and \(\text{FeF}_2\) as about 28-32 \(\frac{cm^3}{mole}\), the potential effect on the density measurement of the FMgNaK salt is estimated conservatively as 0.2% error.

The repeatability of experiment can be estimated from the standard error of the three sets of density measurements. The average standard error in the predicted density from the linear fit is \(2.09 \frac{kg}{m^3}\). This standard error equates to 0.1% of the density values measured.
8.3 Characterization Results of the Molten Salt FMgNaK and Discussion

8.3.1 Note on Simulation Equilibration

Nineteen of our twenty simulations equilibrated in the allotted timeframe, however one simulation at 850 °C was not equilibrated at the end of our 40 ps simulation period. This simulation was not used in our analysis. Due to this issue, the diffusion coefficient values for 850 °C will not have error bars.

8.3.2 Density

There is little experimental literature on the properties of FMgNaK, including relatively straightforward properties such as density. Addressing this lack, we present an experimental correlation for FMgNaK density using techniques described in Section 8.2.2 above. We used this correlation to benchmark our AIMD densities. We compare our experimental and simulation densities to an additive molar volume estimate for the mixture based upon the densities of the binary salt components, MgF\textsubscript{2}, NaF, and KF over the range of temperatures explored. The calculation of the additive density model is described in Appendix B of this forthcoming work but is not included here. This method has been found to agree well with experimentally measured densities in fluoride salts\textsuperscript{15, 18, 155}. We compare simulation and experimental densities, as well as these additive volume density estimates across our temperature range in Figure 8-2.
The linear fits for FMgNaK density shown in Figure 8-2 are listed in Table 8-2 and used in Equation 8-7.

\[
\rho \left[ \frac{kg}{m^3} \right] = a \cdot T[K] + b
\]  

(8-7)

where \( \rho \) is the density, and \( T \) is the temperature in Kelvin. As shown in Figure 8-2, our AIMD density values agree with additive volume density models. The density values are in general agreement with experimental and additive models, though a slight offset was observed in our simulations, being consistently below experimental and additive density models.
Table 8-2: Coefficients of the linear density models. The additive model was calculated from a weighted average of molar volumes for KF, MgF₂, and NaF from Cantor et. al\textsuperscript{180}.

<table>
<thead>
<tr>
<th>Model</th>
<th>( a ) (kg/m(^3)·K)</th>
<th>( b ) (kg/m(^3))</th>
<th>Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>-0.6565</td>
<td>2737</td>
<td>973-1273</td>
</tr>
<tr>
<td>Simulated</td>
<td>-0.4810</td>
<td>2502</td>
<td>1023-1273</td>
</tr>
<tr>
<td>Additive</td>
<td>-0.6318</td>
<td>2711</td>
<td>973-1273</td>
</tr>
</tbody>
</table>

The general agreement between density models shown above enables us to study properties difficult to observe or measure experimentally.

8.3.3 Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) for FMgNaK was calculated using densities throughout our temperature range as described in Section 8.2. The slope of the line fitted to all our CTE values was \(6.09 \times 10^{-8} \text{ K}^{-2}\), and our values had a range of \(1.60 \times 10^{-5} \text{ K}^{-1}\), suggesting negligible temperature dependence. The reported CTE value was calculated at 800 °C and averaged between our two simulations at that temperature. In the absence of an experimentally determined CTE value for FMgNaK, we validate our value using the molar-weighted average CTE of NaF, KF, and MgF₂. NaF, KF, and MgF₂, were measured at 1122 °C, 965 °C, and 1417 °C, respectively\textsuperscript{181}. This resulted in an approximated CTE of 3.27 K\(^{-1}\). However, it should be noted that the CTE is dependent on structure, which will change when these salts are mixed, so this average is intended merely as a general estimate to benchmark our values. Our simulations reported a CTE of \(2.46 \pm .070 \text{ (K}^{-1} \times 10^{-4}\text{)}\), where the error bounds represent a 95% confidence interval.
In general, CTE values from AIMD simulations have consistently been reported as lower than those found in experimental measurements\textsuperscript{123}. This caused an approximate downward shift of as much as $1.0 \times 10^{-4}$ K\textsuperscript{-1} in one study of the CTE of FLiNaK\textsuperscript{55}. Our findings agree with the simulation shift suggested by Woodward et al.\textsuperscript{123} and Nam et al.\textsuperscript{55}

### 8.3.4 Structural Information

The structural data for FMgNaK is summarized in Table 8-3, Table 8-4, and Figures 3-7. AIMD simulation values for FMgNaK’s average bond length (first-peak radius), coordination number, and first peak height are compared with experimental values of FLiNaK due to a similar chemical makeup and to compare the effects of MgF\textsubscript{2} and LiF. Structural properties of FMgNaK are also compared with the properties of FMgNaK’s binary components (MgF\textsubscript{2}, NaF, and KF) to compare structural changes that occur as a result of combining the binary components.

![Figure 8-3: Snapshot of AIMD trajectory for FMgNaK at 1073 °C. Colors green, orange, blue, and purple correspond to elements F, Mg, Na, and K, respectively.](image-url)
We determined first-shell coordination numbers by integrating the RDF from zero to its first minimum. RDFs were generated for each of our equilibrated simulations. 95% confidence intervals for structural values across our temperature range deviated by less than 2%, suggesting negligible structural temperature dependence. Table 8-3 reports the average values of our simulations at 1000 °C.

Compared to FMgNaK’s constituent binary salts, FMgNaK’s coordination number for Na-F increases, yet this increase is less than the increase for K-F. However, the first-peak radius of Mg-F, Na-F, and K-F remained within 5% of the binary salt experimental values\(^{182}\). The coordination number likely increased less in Na-F than K-F because Na\(^+\) ions are more electronegative than K\(^+\) ions\(^{183}\). While Mg\(^{2+}\) ions are even more electronegative than Na\(^+\) ions\(^{183}\), the ratio of anion to cation in FMgNaK (49:46) is much lower than the ratio in pure MgF\(_2\) (2:1), so the Mg-F coordination in pure MgF\(_2\) is likely higher than observed in FMgNaK.

When comparing the Mg-F and Li-F first-peak radii, our analysis revealed a wider first-peak radius in the Mg-F pair than the Li-F pair. This may be due to the Mg\(^{2+}\) ions having a greater coordination number than the Li\(^+\) ions. The first-peak radius of the F-F pair was larger in FMgNaK than in FLiNaK as well. Our measurement reports much greater coordination numbers for F-F in FMgNaK than in FLiNaK. A similar AIMD experiment was performed on the structure of FLiNaK which noted experimental techniques that measure coordination number underrepresent negative ion pairs.\(^1\) This underrepresentation is a trend we observe in our results as well\(^1\). Frandsen et al. reported a coordination number for F-F of only 11.2 in FLiNaK using AIMD\(^1\), but with a much smaller coordination shell radius than was observed in our simulations.

Due to the systemic underrepresentation errors in experimental measurements of coordination
number we trust the greater values reported in AIMD\textsuperscript{1}. Na-F and K-F first-peak radii remained relatively unchanged between FMgNaK and FLiNaK.

Table 8-3: Comparison between the first-peak radius and coordination number found in our AIMD simulations at 800 °C with those found experimentally in similar salts. We should note that all experimental values for binary salts are the same as those cited by Nam et al. in their simulation study of FLiNaK and FLiBe.\textsuperscript{98}

<table>
<thead>
<tr>
<th>Ion Pair</th>
<th>First-peak height of FMgNaK</th>
<th>First-peak radius (Å)</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FMgNaK (AIMD)</td>
<td>Binary Salts (Lit.)</td>
<td>FMgNaK (AIMD)</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}–F\textsuperscript{−}</td>
<td>11.7</td>
<td>1.95</td>
<td>–</td>
</tr>
<tr>
<td>Na\textsuperscript{+}–F\textsuperscript{−}</td>
<td>4.64</td>
<td>2.25</td>
<td>2.30\textsuperscript{b}</td>
</tr>
<tr>
<td>K\textsuperscript{+}–F\textsuperscript{−}</td>
<td>3.20</td>
<td>2.55</td>
<td>2.6\textsuperscript{b}</td>
</tr>
<tr>
<td>F\textsuperscript{−}–F\textsuperscript{−}</td>
<td>1.55</td>
<td>3.55</td>
<td>–</td>
</tr>
<tr>
<td>Li\textsuperscript{+}–F\textsuperscript{−}</td>
<td>–</td>
<td>–</td>
<td>1.85\textsuperscript{b}</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}–Mg\textsuperscript{2+}</td>
<td>4.17</td>
<td>3.45</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data for FLiNaK from our previous AIMD study, which was well-validated by neutron diffraction experiment \textsuperscript{1}

\textsuperscript{b} Experimental data for binary salts from Ohno et al.\textsuperscript{182}

\* We were unable to find literature values for coordination numbers or first peak radii of MgF\textsubscript{2}

Figure 8-4: Radial distribution functions (RDF) of FMgNaK at 800 °C. This analysis was performed on each simulation to check for temperature dependence, and variance across temperatures was minimal.
In studies of FLiBe, Be-F chaining greatly influences the properties of FLiBe\(^{92}\). For example, the viscosity sharply increases as the concentration of Be\(^{2+}\) ions increase. Although the eutectic composition of molten salts is typically chosen for the lowest possible operating temperature, FLiBe’s eutectic composition is undesirable due to the effect of beryllium chaining on viscosity\(^{92}\). Alternate compositions and/or network-breaking cations\(^{92}\) must be employed to counteract this chaining effect in FLiBe.

Mg–Mg distances below 4.0 Å were used to classify chaining events. This cutoff was chosen because it is approximately the distance of 2 Mg-F bonds and a similar distinction was used in defining beryllium chaining in FLiBe\(^{92}\). This made chained magnesium easily distinguishable from unchained magnesium, which consistently had a Mg–Mg distance of at least 5.0 Å.

We observed Mg-F-Mg chaining in 52.6% of our simulations, suggesting the effect of Be-F-Be chaining in FLiBe may also occur in FMgNaK with Mg. As shown in Figure 8-5, the Mg of simulation index 47 (Mg\(_{47}\)) and Mg\(_{48}\) remained closely bonded to F\(_{32}\) from 15 ps until 27 ps. In this simulation at 800 °C, F\(_{32}–\text{Mg}_{47}\) and F\(_{32}–\text{Mg}_{48}\) bonds were 2.11 Å and 2.20 Å, respectively. The distance between Mg\(_{47}\) and Mg\(_{48}\) was 3.43 Å, well below two Mg-F bond lengths, suggesting that the chaining does not occur linearly. Indeed, a visual inspection of the chaining events observed in all equilibrated simulations shows octahedral Mg-F complexes sharing three F\(^-\) ions, as shown in Figure 8-6. This suggests that the chaining occurs along an octahedral face, and not an edge or a vertex of the octahedral.
After sharing F$_{32}$ for over 12 ps, the distances between F$_{32}$–Mg$_{48}$ and Mg$_{47}$–Mg$_{48}$ dramatically increased at 27 ps. These finding suggest that Mg-F-Mg chaining occurred between two of the Mg$^{2+}$ ions, and at 27 ps Mg$_{48}$ separated from F$_{32}$, breaking the chaining event.

The occurrence of a chain-disruption in such a short simulation, coupled with the very low concentration of Mg in FMgNaK, make it very unlikely that Mg chaining will have a strong impact on thermophysical properties of the salt. However, it should not be dismissed that so many simulations involved the formation of a Mg-F-Mg complex, as this indicates two phenomena. First, Mg$^{2+}$ has a strong preference for speciation with other Mg$^{2+}$ ions, so at higher concentrations of MgF$_2$, MgF$_2$-NaF-KF salts would very likely undergo significant magnesium
chaining. Second, this speciation of Mg\(^{2+}\) will likely have impacts on the diffusion of Mg\(^{2+}\) in the salt.

Similar Mg–F–Mg chaining occurred in 10 out of our 19 equilibrated simulations. The distribution of these potential chaining events across our sample temperatures is given in Table 8-4. No chain involving 3 Mg\(^{2+}\) ions was observed in any simulation.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Fraction of Simulations with Chaining</th>
<th>Average Mg–Mg distance (Å) in Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1023</td>
<td>33.3%</td>
<td>3.45</td>
</tr>
<tr>
<td>1073</td>
<td>100%</td>
<td>3.50</td>
</tr>
<tr>
<td>1123</td>
<td>100%</td>
<td>3.25</td>
</tr>
<tr>
<td>1173</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>1223</td>
<td>50%</td>
<td>3.45</td>
</tr>
<tr>
<td>1273</td>
<td>66.7%</td>
<td>3.58</td>
</tr>
</tbody>
</table>

In FLiBe, the beryllium chaining occurs with negligible impact to the F\(^{-}\) coordination of Be\(^{2+}\). In FMgNaK, the F\(^{-}\) coordination of Mg\(^{2+}\) appears to shift. In unchained magnesium ions, the fluoride coordination appears to typically be five, and is structured as shown in Figure 8-6. However, in a magnesium chaining event, the fluoride coordination is consistently six, as shown in Figure 8-7.
Figure 8-6: An example of Mg-F chaining observed at 750 °C. The third Mg2+ ion, Mg92, was completely dissociated and did not participate in Mg-F chaining.

Figure 8-7: An example of a Mg monomer, observed in FMgNaK at 750 °C. It should be noted the simulation used in this figure is a separate simulation than that of Figure 8-6, though both were performed at 750 °C.
8.3.5 Self-Diffusion Coefficients

We analyzed the self-diffusion coefficients of F−, Mg2+, Na+, and K+ ions from our AIMD simulation trajectories using the Green-Kubo method described in Section 8.3.5. Several of our calculated diffusion coefficients exhibited negative values. Negative diffusion coefficients suggest migration towards, rather than from, their point of interest\textsuperscript{184}. This was observed predominantly in the Na ions. In the case of negative self-diffusion coefficients, the ion tends to concentrate rather than disperse. This phenomenon leads to an increase in structuring among ions, however this structural behavior is not sustainable in our finite systems. Due to an error in our calculations, our SDC values are not reported. The discrepancy in negative diffusion in certain species is not expected to resolve with more accurate computations.

We believe the negative values of diffusivity could also be a result of wide variances in data, as most of our negative self-diffusion coefficients have standard deviations extending above the x-axis.

The large variance of our diffusion values may be an artefact of AIMD simulations. AIMD’s energy surfaces are accurate and effective in determining many properties, but their computational expense lends to small system sizes and brief simulation times, on the order of tens of picoseconds. This leads to relatively few diffusion events, causing large statistical variance. To achieve diffusion coefficients with 52% relative standard deviations (RSD), AIMD would need to run for at least 1000 ps to contain enough diffusion events, which is well outside practical limits for these simulations\textsuperscript{172}. These findings and a detailed study on diffusion variance in AIMD were reported by He et al.\textsuperscript{172}, who predict diffusion variance as large as an one or two orders of magnitude for simulations unable to meet minimum levels of diffusion events\textsuperscript{172}. This
agrees with the variance reported in Figure 8-2 and may explain why our data reported unusual values.

With ample simulation time, additional diffusion events should reduce the variance in the self-diffusion coefficients. If the true values are positive, this would indicate the need for longer simulations in AIMD to reduce variance and capture diffusion behavior. However, if the true value converges towards a value at or below zero, this could indicate structural phenomena such as ion clusters\textsuperscript{184} or simply negligible diffusion among ions. We believe these potential effects warrant additional study, and we plan to further investigate this phenomenon to better understand diffusion in FMgNaK salts.

8.3.6 Bader Charge Analysis

We calculated partial charges for the ions in FMgNaK for each equilibrated simulation using the Bader charge analysis described in Section 8.3.6 and those charges are listed in Table 8-5. The average Bader volume of each ionic species is also included in Table 8-5.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Bader Charge</th>
<th>Bader Volume (Bohr(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsuperscript{-}</td>
<td>-0.875 ± 0.00079</td>
<td>168 ± 5.0</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>1.76 ± 0.0021</td>
<td>42.1 ± 0.98</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>0.891 ± 0.00064</td>
<td>78.9 ± 1.4</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>0.865 ± 0.0013</td>
<td>170 ± 4.1</td>
</tr>
</tbody>
</table>
8.4 Conclusions

In this work, we employed AIMD simulations to predict structure, charge, and thermophysical properties of FMgNaK. Density predictions were compared to experimental measurements and affirmed the validity of our AIMD simulations in modeling FMgNaK at high temperatures. Charge, structure, and thermophysical properties of FMgNaK such as density and coefficient of thermal expansion were generally in good agreement with experimental measurement as well as the additive volume density approximations given in existing literature\(^{180}\) using each of its constituent binary salts. While our simulations suggest the presence of Mg-F chaining, we do not believe its effects to have a large impact on the properties of FMgNaK due to the low concentration of Mg in the salt. Large variance in our diffusion values confirm AIMD’s short simulation time and small box size are not ideal for diffusion calculations. The AIMD simulations also provided the first thermophysical and structural values for FMgNaK, yielding a more accurate source of properties than a weighted average of values from FMgNaK’s constituent salts.

This study provides thermophysical properties of FMgNaK and demonstrates that despite the computational expense of AIMD, AIMD can successfully model thermophysical properties of high temperature fluoride salts. We plan to further explore the diffusion phenomena of molten FMgNaK to determine the root cause of our negative values and observed diffusive behavior.

An important finding that was not submitted for publication is that lengthy simulation times are needed for structural equilibration, much longer than many of our contemporaries have previously utilized\(^{54, 55, 74, 92, 93, 98, 99}\). As shown in Figure 8-8 and Figure 8-9, the ordering of sodium over time proceeds from relatively dispersed to distinctively ordered on one side of the box, suggesting that cation-cation interactions are relatively important in considering solute-salt
interactions and behavior. This behavior was observed in the majority of FMgNaK simulations in this study. This relationship is explored further in Section 10.

Figure 8-8. Snapshot of the simulation of the molten salt FMgNaK at 1073 K. This snapshot was taken 15 ps into the simulation. Fluoride ions are green, potassium ions are purple, sodium ions are blue, and magnesium ions are yellow.

Figure 8-9. Snapshot of the simulation of the molten salt FMgNaK at 1073 K. This snapshot was taken 40 ps into the simulation. Fluoride ions are green, potassium ions are purple, sodium ions are blue, and magnesium ions are yellow.
9 COMPLEXATION OF MOLYBDENUM IN MOLTEN FLUORIDE SALT

Having successfully demonstrated that our methodology produced sufficiently accurate simulation results on a clean molten salt system, we then expanded into more complex systems involving fuel, fission products, and corrosion products. Our primary focus initially was on the fission product Mo-99. Our published work on Mo complexation included only results on molten FLiNaK salt, as follows.

9.1 Introduction to Molybdenum Complexation in molten FLiNaK

Online extraction of fission products, such as the medical isotope Mo-99, is a key advantage of the proposed molten salt nuclear reactor design. The chemical and structural behavior of Mo while solvated in fluoride salt has been relatively unknown. Ab initio molecular dynamics (AIMD) simulations were employed to examine the behavior of molybdenum in the molten salt FLiNaK (LiF-NaF-KF) for oxidation states between 0 and 6+. Mo complexation was found to vary with Mo oxidation state, with lower oxidation states tending to result in complexes with more molybdenum ions. Complexes containing multiple Mo ions were observed for all Mo oxidation states studied except 5+ and 6+. A relationship between the solubility of a complex and electronic isolation of a complex in a molten salt is explored using the Bader atoms in molecules (AIM) electron density partitioning scheme, with more volatile complexes exhibiting greater electronic isolation. The impacts of UF₄ and H₂O on the predominant molybdenum
species are also considered. While no impacts on Mo behavior by UF₄ were observed, Mo-O interactions may inhibit the formation of complexes containing multiple Mo ions.

In molten salt reactors (MSRs), nuclear fission products are formed directly within a molten fluoride or chloride salt. One fission product of particular interest is molybdenum, as the isotope Mo-99 is the predecessor to Technicium-99³⁷, a short-lived isotope used in medical imaging³⁶. If Mo-99 could be isolated from the molten salt solutions circulating through active MSRs, these reactors could serve as a reliable source of the valuable isotope. Therefore, there is considerable interest in predicting the solution chemistry of molybdenum in molten salts.

Molybdenum is a multivalent metal with several available oxidation states, and the stability of Mo in molten salt solution varies with these oxidation states. A similar pattern has been observed in both fluoride and chloride molten salts: Mo(0) precipitates as a solid; Mo(I) and Mo(II) are not stable in solution;¹⁸⁵⁻¹⁸⁹ Mo(III) and Mo(IV) have both been observed to remain stably dissolved within a molten salt melt;¹⁸⁹, ¹⁹⁰ and Mo(IV), Mo(V), and Mo(VI) have been observed to leave solution as a vapor in the form of MoX₄, MoX₅, and MoX₆, with MoX₅ and MoX₆ far more common in the vapor phase¹⁸⁶, ¹⁸⁹⁻¹⁹².

Given these trends, studies of Mo in molten salt have often focused on Mo(III). However, there is some indication that Mo(III) in molten sat may undergo a disproportionation reaction. In the late 1960s and early ‘70s, researchers associated with the original Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Lab found that when MoF₃ was dissolved in the molten fluoride salt FLiBe (66.7-33.3mol% LiF-BeF₂), some fraction of Mo left solution as Mo(0) metal and as volatile higher-valence Mo fluorides (MoF₅ and MoF₆, sometimes MoF₄)¹⁸⁵, ¹⁸⁶, ¹⁸⁹, ¹⁹¹⁻¹⁹³. Similar Mo(III) behavior has been found in the molten salt FLiNaK (46.5-11.5-42 mol% LiF-NaF-KF) ¹⁹⁰ as well as the molten chloride salt KLiCl (55.8-44.2 mol% LiCl-KCl),
with multiple authors observing the decomposition of Mo(III) in KLiCl into Mo metal and a vapor, typically presumed to be MoCl$_5^{194-196}$.

In 1967, the apparent kinetics of Mo(III) disproportionation in KLiCl led Senderoff and Mellors$^{195}$ to speculate that much of the dissolved molybdenum existed in the form of a di-nuclear Mo complex (Mo$_2$Cl$_9^{3-}$) that is relatively stable in solution and does not undergo disproportionation, in equilibrium with a mononuclear complex (MoCl$_6^{3-}$) which does. However, spectroscopic studies in more recent decades have not identified any poly-nuclear Mo complexes in KLiCl solution, instead finding MoCl$_6^{3-}$ to be the only clearly-detectable species.$^{187, 188, 197, 198}$ This has led some to suggest that the disproportionation reported by earlier studies did not represent a homogenous reaction, with Mo interacting solely with itself, but instead indicated Mo reacting with oxide contaminants$^{199}$.

Still, it is difficult for spectroscopic studies of molten salts to definitively rule out the presence of any given Mo species at high temperatures$^{187}$, making di-nuclear or even tri-nuclear Mo solution complexes a possibility. Even less is known about the solution behavior of oxidation states of Mo other than Mo(III).

This work uses ab initio molecular dynamics (AIMD) simulations based on density functional theory$^{112, 200}$ to examine the behavior of molybdenum within molten FLiNaK, a commonly-proposed salt for MSR applications. In particular, this study focuses on the complexation of molybdenum when it is allowed to interact with itself or with contaminants such as uranium or water.
9.2 Methodology for AIMD Simulation of Molybdenum Complexation in Molten FLiNaK

9.2.1 Preparation of the Simulation Cell

FLiNaK is defined as 46.5-11.5-42 mol\% LiF-NaF-KF. It is impossible to achieve these molar proportions exactly with less than 400 atoms, which for ab initio molecular dynamics would require significant computational cost. As such, the simulation cells used in this study had slightly different molar proportions than would a macroscopic sample of FLiNaK.

This study is divided into two parts: the first examining the complexation of Mo of different oxidation states, and the second examining the effect of contaminants on the complexation of Mo(III). In the first part, 13 Li atoms, 3 Na atoms, 12 K atoms, and 28 F atoms (56 total) were added to a simulation cell to account for the bulk solvent, corresponding to a mixture of 46%-11%-43% LiF-NaF-KF. Three Mo atoms were then added (this number was chosen because we were particularly interested in whether it was possible for di-nuclear or tri-nuclear molybdenum complexes to form).

Along with the Mo atoms, enough F atoms were added to determine the desired Mo oxidation state for each simulation cell—e.g. 3 F atoms for each Mo atom for a molybdenum oxidation state of Mo(III). This technique has been used to study other solutes with multiple possible oxidation states such as Cr in FLiNaK and FLiBe\textsuperscript{98}. However, since in our case each simulation cell contained multiple Mo atoms, it is possible that the simulation would generate multiple different Mo oxidation states in the same cell—e.g. 2 Mo atoms and 6 F atoms resulting in one Mo(II) and one Mo(IV). This result did not occur in any of our simulations. These simulations were conducted at 950K as several experimental density correlations have been reported for FLiNaK at this high temperature,\textsuperscript{31} allowing us to check the simulated density of pure FLiNak to the experimental values (see Section 9.2.2).
In order to check for artifacts that might arise from including only three atoms in a simulation cell, we also ran one box with six Mo(III) atoms. Keeping the number of solvent atoms the same in this simulation would have radically increased Mo concentration, and so this cell contained 23 Li atoms, 6 Na atoms, 21 K atoms, and 50 F atoms (100 total), corresponding to a mixture of 46%-12%-42% LiF-NaF-KF. This box was simulated at 500°C (773K).

For the second part of the study, examining the effect of contaminants, the larger simulation cells were again used with 100 atoms of FLiNaK solvent, as described above. To this solvent was added three Mo(III) and a contaminant: either 5 UF₄ molecules or 6 H₂O molecules.

Each simulation cell was prepared following the method from Bengtson et al⁵⁵ and previously used by Nam et al⁹⁸ for molten salts. First, all atoms (including both salt and solutes) were randomly inserted in a simulation cell using the Packmol software package¹²⁴. Then, the system underwent a brief (10 ps) classical molecular dynamics simulation using a Born-Mayer-Huggins potential model as employed the LAMMPs simulation package²⁰¹ in order to obtain a more energetically favorable initial configuration for the AIMD simulations and thereby reduce computational costs.⁵⁹ The potential parameters used in the LAMMPS MD equilibration were taken from Salanne et al⁵⁰, though the polarizable portion of that force field was not implemented. Mo potential parameters were based on the trivalent cation parameters presented by the same group²⁰². Because this classical MD step is meant merely to obtain a more energetically favorable initial configuration for the AIMD equilibration, the exact parameter choice is not critical⁹⁸, and the LAMMPS simulation is never assumed to have a high level of physical accuracy.
9.2.2 AIMD Details

Ab initio molecular dynamics (AIMD) based on density functional theory (DFT) were performed using the CP2K software package\textsuperscript{120, 160}. The AIMD methods employed were the same as in a previous study, in which they were found to predict FLiNaK densities and pair distribution structures extremely close to experiment\textsuperscript{1}.

AIMD calculations utilized the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\textsuperscript{203}, a form of general gradient approximation (GGA). The Gaussian and plane waves method (GPW) was used, in which wave functions are represented by atom-centered Gaussian orbitals and the electron density is represented by plane waves\textsuperscript{122, 161, 204}. Within this framework, all atoms were modeled using DZVP-MOLOPT-SR-GTH basis sets\textsuperscript{90, 91, 163} with core electrons treated with Goedecker-Teter-Hutter pseudopotentials\textsuperscript{90, 91, 120, 164, 165}. The plane-wave energy cutoff was set at 2000 Ry and the relative cutoff at 120 Ry. Simulations were performed in the NPT ensemble using the canonical sampling through velocity rescaling (CSVR) thermostat\textsuperscript{166} with a timestep of 0.5 fs. Corrections for Van der Waals dispersion forces were not included, as a previous study of FLiNaK using the same AIMD methods described here found that including dispersion corrections resulted in less accurate density predictions compared to experimental correlations\textsuperscript{1}. Due to the open-shell nature of molybdenum and its oxidation states, the Kohn-Sham calculations utilized the spin-unrestricted formalism for controlling electron spin\textsuperscript{205}.

Each AIMD simulation was equilibrated for a minimum of 15 ps. While this equilibration length is ample in comparison to other AIMD works\textsuperscript{206-209}, the liquid density of several simulations was found to fluctuate significantly even after the total energy of the simulation converged to within four significant figures, as shown in Figure 9-1. Relatively large density fluctuations compared to energy fluctuations are common in simulated molten salt systems due
to their low bulk moduli\textsuperscript{98}. For this reason, after the initial 15 ps of equilibration, each simulation was allowed to run until the average density over 5 ps was within 2\% of the average density of the previous 5 ps. That 10 ps segment was taken as the “production run” and analyzed to produce the results reported here. The maximum total simulation time required to meet this criteria was \(~50\) ps, (for cells containing Mo(0)), while the average time for all simulations was 27.75 ps.

The average equilibrated cubic cell lengths were 10.6 Å, and 12.8 Å for the cells containing 56 and 100 Flinak atoms, respectively. At the beginning of the AIMD equilibration step, the average minimum distance between Mo atoms was 3.44 Å for the smaller (~10.56 Å) boxes and 4.01 Å for the larger (~12.77 Å) boxes. Most Mo-Mo bonds observed throughout the study formed quickly, with Mo atoms coming into contact and binding to each other within three picoseconds of the beginning of the AIMD equilibration. Once formed, Mo-Mo bonds remained stable, and all existed throughout the 10-ps production run for each simulation cell.

It should be noted that the atomic fractions of molybdenum in these simulations (~0.04-0.05) are large compared to what would be found in an actual molten salt reactor (reproducing these realistic concentrations would require cell sizes which would be prohibitively expensive for AIMD). It is possible that the Mo complexes formed in this simulation would not form in lower-concentration solutions; however, there is some evidence that low concentrations of Mo in molten salts may undergo disproportionation through a homogenous reaction\textsuperscript{185, 186, 189, 191, 193}. If true, this would suggest that Mo atoms do come into close contact with each other and interact, even when present in relatively low concentrations.
Figure 9-1. The total simulation energy in Hartrees (top) and the simulation liquid density (bottom) as functions of time for a simulation containing Mo(III) in FLiNaK at 500℃.

9.2.3 Structure Analysis

Radial distribution functions (RDFs) were generated using Visual Molecular Dynamics (VMD) software tools\textsuperscript{210}, which for periodic boundary conditions can calculate normalized RDFs
to a range of $r \leq \frac{\sqrt{2}}{2} L$, where $L$ is the length of the periodic cell. Given the small box size necessitated by AIMD, we believe an extended RDF range gives a better picture of the salt structure around dissolved Mo, though the statistics of the RDF are of poorer quality past a length of half the box size. Each RDF was averaged over the 10 ps production run portions of the simulations.

As an important element of this analysis was observing which solution complexes form under which conditions, it was necessary to find a non-arbitrary method of defining a “complex.” A “molybdenum complex” in this work is defined as a molybdenum atom or group of bonded molybdenum atoms together with all the fluoride atoms in the first solvation shell of those molybdenums.

### 9.2.4 Charge Analysis

Bader charges$^{211}$ were calculated for all atoms. Bader charges for each atom in a DFT system are found by defining a Bader volume around each nucleus, with the volume surface following local minima in the electron density. The electron density is then integrated over the Bader volume and added to the charge of the nucleus to find the Bader charge. Here, Bader charges were determined using code shared by the Henkleman group$^{104}$ which analyzes the electron density cube files created by CP2K. These cube files were printed out every 50 fs of simulated time over ~1.5 ps of production run. Bader charges are reported as time-averaged values over the entire production run.
9.3 Simulation Results and Discussion

9.3.1 Molybdenum Complexation in FLiNaK

Figure 9-2 and Table 9-1 show the complexes that form when three molybdenum atoms of varying oxidation states are placed in a FLiNaK simulation cell at 950K. All of these complexes were stable over 10 ps of simulation time, and show a shifting pattern with increasing Mo valence: Mo of valence Mo(0) and Mo(I) formed tight trinary compounds with little interaction with fluoride anions; Mo(II), Mo(III), and Mo(IV) formed one mono-nuclear and one di-nuclear complex; and Mo(V) and Mo(VI) formed three separate mono-nuclear complexes. No tri-nuclear complexes were formed. The simulation cell containing six Mo(III) atoms formed two di-nuclear complexes and mono-nuclear complexes, confirming that both configurations are possible and are not an artifact of the number of Mo atoms simulated.

<table>
<thead>
<tr>
<th>Mo Formal Oxidation State</th>
<th>Complexes Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(0)</td>
<td>Mo₃</td>
</tr>
<tr>
<td>Mo(I)</td>
<td>Mo₃⁺³</td>
</tr>
<tr>
<td>Mo(II)</td>
<td>MoF₄⁻², Mo₂F₈⁻⁴</td>
</tr>
<tr>
<td>Mo(III)</td>
<td>MoF₆⁻³, Mo₂F₈⁻²</td>
</tr>
<tr>
<td>Mo(IV)</td>
<td>MoF₆⁻², Mo₂F₁₀⁻²</td>
</tr>
<tr>
<td>Mo(V)</td>
<td>MoF⁷⁻²</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>MoF⁷⁻¹</td>
</tr>
</tbody>
</table>

Notably, Mo(III) and Mo(IV) are the most stable oxidation states of molybdenum in molten salt solution, and our results show that these are the only oxidation states which form an
octahedral mono-nuclear complex with six coordinating anions (MoF$_6^ {-3}$ or MoF$_6^{-2}$). Mo(II), Mo(III), and Mo(IV) are also the only oxidation states to form di-nuclear complexes.

![Diagram of Mo(0), Mo(I), Mo(II), Mo(III), Mo(IV), Mo(V), and Mo(VI) complexes](image)

Figure 9-2. Complexes formed by Mo of varying oxidation state in FLiNaK at 950K. Mo is blue and F is green.

We speculate that di-nuclear Mo complexes and mono-nuclear complexes of the form MoX$_6$ are favored by the molten salt environment, and Mo oxidation states which can form these complexes will tend to be more stable in solution. (While spectroscopic studies of Mo in molten
salts are not plentiful, such studies of Mo(III) in the chloride salt KLiCl have found MoCl₆³⁻ to be the only clearly identifiable molybdenum complex²¹².)

Our results do suggest that poly-nuclear complexes similar to those suggested by Senderoff and Mellors¹⁹⁵ can form within a molten salt. However, this in itself is not strong support for the specific molybdenum disproportionation mechanism Senderoff and Mellors proposed. Rather, the formation of these di-nuclear complexes is significant in so far as it indicates that Mo cations in molten salt solution can and do interact with each other, including the sharing of valence electrons, as would be necessary for a disproportionation reaction. That is, the di-nuclear complexes observed here could plausibly act as reaction intermediates. While no such reaction was observed over the timescale of these simulations, we cannot determine from these results whether disproportionation would occur given a larger timescale.

Since all Mo oxidation states from Mo(II) to Mo(VI) form at least one mono-nuclear complex, the mono-nuclear complexes can be directly compared as in the radial distribution functions of F around Mo, shown in Figure 3. The clearest divergence in the RDFs is in the first peak, and so this portion of the RDFs is also shown in detail to aid interpretation. The first peak radius, corresponding to the Mo-F bond distance, varies between Mo oxidation states. For most of the states, this variance follows an expected pattern—the higher the oxidation state of Mo (corresponding to a more positive charge and less electron-electron repulsion), the shorter the first peak distance, indicating more closely bound fluorine anions. However, Mo(IV) and Mo(V) break this pattern, with Mo(IV) having a closer coordination shell than Mo(V). A sharper, narrower peak generally indicates fluorides that are more tightly bound at the indicated distance. The lower oxidation states of Mo here have broader Mo-F peaks, which is reasonable given that these molybdenum atoms will have a less positive charge and thus a weaker ionic attraction to
fluorides. However, Mo(IV) appears to have the sharpest peak, narrower than that of Mo(V) and Mo(VI). Taken together, the Mo-F RDFs suggest a discontinuity of behavior at a Mo oxidation state of IV—the highest oxidation state of Mo known to remain in molten salt solution in significant amounts, and the only oxidation state known to both stay in solution and leave as a volatile halide.

This discontinuity is likely due to the shift in coordination between Mo(IV) and Mo(V): Mo(IV) forms MoF$_6^{2-}$, while Mo(V) attracts negative fluorides more strongly, forming MoF$_7^{2-}$, but with this coordination fluorides crowd each other out and each is less tightly bound. This causes the average Mo-F bond distance to increase, offsetting the decrease in Mo ion size due to the loss of an electron. (It is well-established that the ionic radii of molybdenum and other metals in halide complexes is a function of both oxidation state and coordination number.\textsuperscript{213}) In other words, a shift in coordination causes a qualitative shift in the interaction between Mo and the surrounding anions of the molten salt solvent, likely making it more favorable for the Mo to shed fluorides and leave solution as a neutrally charged volatile compound.

The interaction of the molybdenum complexes with the surrounding salts was examined through Bader charge analysis. Table 9-3 shows the Bader charge of each of the identified Mo complexes (that is, the Bader charge of the central Mo atom or atoms plus the Bader charge of each of the surrounding F atoms.) The rightmost column shows the difference between the complex Bader charge and the formal charge of the complex (calculated from the formal oxidation state of the
Figure 9-3. Mo-F radial distribution functions for all mononuclear molybdenum complexes observed in FLiNaK at simulation temperatures of 950K (top). While the simulation cells analyzed here have an average box length of 10.6 Å, the smallest box has an average length of 10.2 Å, and so the RDFs are shown to a range of \( r \leq \frac{\sqrt{2}}{2} (10.2 \text{ Å}) \), or 7.2 Å (see section 2.3 above). For ease of interpretation, the region from 1.6 Å to 2.5 Å, encompassing the first peak, is shown in detail (bottom).
Table 9-2. Fluoride coordination number for each mononuclear Mo species identified in simulations at 950 K. The fluoride number density weighted integrals of the RDFs shown in Figure 9-3 were evaluated from 0 to 2.8 Å.

<table>
<thead>
<tr>
<th>Mo Formal Oxidation State</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(II)</td>
<td>4.09</td>
</tr>
<tr>
<td>Mo(III)</td>
<td>6.04</td>
</tr>
<tr>
<td>Mo(IV)</td>
<td>6.00</td>
</tr>
<tr>
<td>Mo(V)</td>
<td>6.99</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>7.04</td>
</tr>
</tbody>
</table>

Mo atom and the number of F atoms in the complex.) This difference is a measure of the degree to which the molybdenum complex shares electrons with the surrounding salt environment. A positive number indicates that the complex is (relatively speaking) giving electrons to the salt, while a negative number indicates that the complex is taking electrons from the salt.

A Bader charge on an ion differing from the integer value expected from its formal charge indicates that the ion is sharing electrons with surrounding atoms—it is acting less ioniically and more covalently. In ionic fluids such as molten salts, “covalent” effects amount to ionic polarizations that cause deviations in the charge distributions of valence electrons relative to the simple ionic model, changing the entire ionic environment and affecting salt behavior and properties.\(^\text{214}\) Bader charge, a measure of covalence, therefore also indicates differences in polarization and in the interaction between a solute and its ionic solvent environment. Previous studies on solutes in molten salts have found Bader charge of a complex to correlate with how well the complex is solvated by the cations and anions of a molten salt\(^\text{215}\).
In our case, looking at each type of complex separately (the trinary Mo compounds, the mono-nuclear fluoride complexes, and the di-nuclear fluoride complexes) a general trend appears: a more negative Bader charge – formal charge difference with increasing Mo valence. One exception to this trend is the Mo(II) mononuclear complex which is significantly less positive than the Mo(III) complex. The Mo(II) mononuclear complex has a roughly square planar geometry often seen in transition metals\textsuperscript{216}. This oxidation state is known to be unstable in solution\textsuperscript{185-189}, and Bader analysis yields a key insight why. Given that the number of unpaired d-orbital electrons in Mo(II) is four and the coordination number for Mo(II) is also four, MoF\textsubscript{4}\textsuperscript{2-} is much less a solvated complex and more of a molecule. That the Bader charge – formal charge difference for this molecule is close to zero implies that the interactions between the MoF\textsubscript{4}\textsuperscript{2-} molecule and the salt are relatively non-polarizing. The stable mononuclear complexes Mo(III) and Mo(IV) both have much more positive Bader charge – formal charge differences. This implies stronger polarization occurs between those two mono-nuclear complexes and the salt solvent.

The Mo(V) and Mo(VI) mono-nuclear complexes, on the other hand, have Bader charge – formal charge differences close to zero, indicating very little sharing of electrons with the salt environment. In other molten salts Mo(V) and Mo(VI) are known to leave salt solution as volatile halides. This suggests that these higher-valence molybdenum fluoride complexes, likely less favorable in the salt environment, are also more isolated from that environment. The relationship between solute/solvent electron sharing and solution stability in molten salts should be further explored in future work.
Table 9-3. Bader charges of Mo complexes observed at 950K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mo Oxidation State</th>
<th>Complex Bader Charge</th>
<th>Complex Bader Charge – Formal Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Mo(0)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>*Mo⁺³</td>
<td>Mo(I)</td>
<td>2.11</td>
<td>-0.89</td>
</tr>
<tr>
<td>MoF₄²</td>
<td>Mo(II)</td>
<td>-1.87</td>
<td>0.13</td>
</tr>
<tr>
<td>MoF₆³</td>
<td>Mo(III)</td>
<td>-2.12</td>
<td>0.88</td>
</tr>
<tr>
<td>MoF₆²</td>
<td>Mo(IV)</td>
<td>-1.39</td>
<td>0.61</td>
</tr>
<tr>
<td>MoF₇²</td>
<td>Mo(V)</td>
<td>-1.88</td>
<td>0.12</td>
</tr>
<tr>
<td>MoF₇¹</td>
<td>Mo(VI)</td>
<td>-1.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>Mo₂F₈⁴</td>
<td>Mo(II)</td>
<td>-3.58</td>
<td>0.42</td>
</tr>
<tr>
<td>Mo₂F₈²</td>
<td>Mo(III)</td>
<td>-1.83</td>
<td>0.17</td>
</tr>
<tr>
<td>Mo₂F₁₀²</td>
<td>Mo(IV)</td>
<td>-2.34</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

*The Mo(I) complex definition is somewhat arbitrary. The complex is solvated by fluorides (CN of 2.67), but the fluoride coordination lacks the clear structure found in the other complexes and undergoes frequent fluoride-fluoride exchanges, thus the fluorides were excluded from the complex.

9.3.2 Contaminate Effects on Mo Complexation

UF₄ does not appear to affect the complexation of Mo(III). As seen in Figure 9-4, Mo(III) formed the same mono-nuclear and di-nuclear complexes as when uranium was not present, even at the much higher temperature. Water, on the other hand, had a dramatic effect on molybdenum complexation. As shown in Figure 9-5, one of the three Mo(III) atoms present formed a MoF₆³ complex (as in the case with no contaminates) while the other two formed molybdenum fluoro-oxides. That no di-nuclear molybdenum complex formed suggests a preference for Mo(III) to
form oxides over di-nuclear complexes. We speculate that water contamination of a molten salt (which is common) would make it less likely for di-nuclear Mo complexes to be formed or detected.

The MoF$_6^{3-}$ complex pictured in Figure 9-5 was stable over 10 ps of simulation time. One of the molybdenum fluoro-oxides formed, an MoOF$_5^{-4}$ complex with similarly octahedral geometry, started the production run period as MoF$_5$(H$_2$O)$_2^-$, but the hydroxide group was twice deprotonated during the simulation. The third Mo(III) atom start the production run as MoO(OH)F$_4^{-4}$, another octahedral complex, but it destabilized when a solvent fluoride reacted with the hydrogen on the hydroxide group, forming HF. Without that hydrogen, the molybdenum complex rejected one of its fluoride atoms, forming the trigonal bipyramidal structure MoO$_2$F$_3^{-4}$ and maintaining an overall charge of -4. Figure 9-6 shows all of the molybdenum fluoro-oxides present initially and after 10 ps of production run simulation time.

The behavior of the Mo-O bond differed in each of these complexes, as illustrated in Figure 9-7, showing radial distribution functions for the Mo-O pairs. To emphasize the trend in Mo-O interactions, the RDFs for the fluoro-oxide complexes were computed twice; once over the entire 10 ps of the production run and once using data from only the last 1 ps of the simulation. In the MoOF$_5^{-4}$ complex, this allows us to see three distinct RDF peaks for the Mo-O interaction. The 1 ps Mo-O RDF exhibits two distinct peaks, as the second deprotonation of the hydroxide group occurs within this time frame. Thus, the final structure corresponds to the Mo-O peak at 1.65 Å.

The initial MoO(OH)F$_4^{-4}$ structure exists for ~9 ps of the production run, thus the PRF for the entire 10 ps has two distinct peaks; one for each oxide group. The final MoO$_2$F$_3^{-4}$ complex, on the other hand, has a single, sharp Mo-O RDF peak in the 1 ps RDF indicating a single stable
bond distance, as the deprotonation of this complex’s hydroxide group occurs just before the last
1 ps of simulation.

Figure 9-4. Molybdenum complexes observed in FLiNaK at 900°C in the presence of UF4; U is yellow, Mo blue, F green.

Figure 9-5. Molybdenum complexes observed in FLiNaK at 667°C (940K) in the presence of water. Mo is blue, F green, H white and O red.

9.4 Published Conclusions

In this work, ab initio molecular dynamics (AIMD) simulations were employed to
examine the behavior of Mo of various oxidation states in molten FLiNaK. The molybdenum
complexes that formed differed by Mo oxidation state, with Mo of valence Mo(0) and Mo(I)
forming Mo₃ compounds with little interaction with fluoride anions, Mo(II), Mo(III), and Mo(IV) forming

Figure 9-6. Molybdenum fluoro-oxides formed in FLiNaK at 940K (667°C): a) Mo(H₂O)F₅⁻²/MoOF₅⁻⁴, and b) MoO(OH)F₄⁻⁴/MoO₂F₃⁻⁴ before and after the hydrogen(s) on the hydroxide groups are taken by solvent ions.

Figure 9-7. RDFs for Mo-O pairs in FLiNaK at 940K (667°C). The RDFs shown are for the MoF₅O⁴⁻ and the MoF₃O₂⁴⁻ complexes. The solid lines represent the RDFs generated using only the last 1 ps of simulation data, while the dashed lines represent the RDFs generated using the entire 10 ps of production run.

101
both mono-nuclear and di-nuclear molybdenum fluoride complexes, and Mo(V) and Mo(VI) forming only mono-nuclear complexes. As Mo(III) and Mo(IV) are known to be the most stable forms of Mo in molten halide salts, we speculate that the complexes formed by these oxidation states (MoF$_6^{-3}$, Mo$_2$F$_8^{-2}$, MoF$_6^{-2}$, Mo$_2$F$_{10}^{-2}$) are relatively favored by the salt environment. The di-nuclear complexes formed could plausibly act as intermediates in a molybdenum disproportionation reaction, though no such reaction was actually observed over the timescale of the simulation.

The Mo(IV) mono-nuclear complex, MoF$_6^{-2}$, appears to behave differently than other mono-nuclear complexes, with shorter Mo-F bond distances and greater electron-sharing with the salt environment than would be expected from observed trends with oxidation state. On the other hand, the Mo(V) and Mo(VI) mononuclear complexes, MoF$_7^{-2}$ and MoF$_7^{-1}$, exhibited almost no electron-sharing with the salt environment. As Mo(VI) is the highest Mo oxidation state known to remain stably dissolved in molten halide salts, while Mo(V) and Mo(VI) exit solution as volatile halides, this suggests a relationship between solute-solvent electron sharing and solution stability within molten salts.

The effect of contaminants on Mo complexation was examined by adding either UF$_4$ or H$_2$O to FLiNaK salt containing Mo(III). The presence of UF$_4$ appeared to have no effect on Mo complexation. In the presence of water, no di-nuclear Mo complexes formed, with molybdenum fluoro-oxides forming instead. It is likely that water contamination of molten salts would prevent di-nuclear molybdenum complexes from forming or being observed.

Overall, this study indicates the molybdenum complexation in FLiNaK varies with Mo valence and is related to the stability of Mo of different states in molten salt solution. Future
studies on the relationship between solution stability and electron sharing between the solute and solvent in molten salts would be of interest.

9.5 Unpublished Results and Inferences

The following sections were removed from the final submitted work on molybdenum complexation which was later published. They do however offer important insights into this overall research work, and so have been included. These portions include molybdenum complexation research in FLiBe and KLiCl, our only chloride salt work completed. They will all suffer for this outrage.

9.5.1 Plane-wave Cutoffs and Van derWaals Dispersion Corrections

In plane-wave DFT, plane-waves basis sets are truncated to only include plane waves corresponding to a kinetic energy below some cutoff value. This cutoff leads to error in computed energy, with larger cutoffs corresponding to smaller error but greater computational cost. In the GPW method as implemented by CP2K, a higher plane-wave energy cutoff means that the electron density will be mapped onto a finer grid. Gaussians are mapped onto a coarser grid defined by a “relative cutoff” value—for example, a “relative cutoff” of 50 Ry means that calculated Gaussian orbitals will have the same resolution as a grid with a plane-wave cutoff of 50 Ry.

Given that the NPT ensemble is known to require higher energy cutoffs than simulations without fluctuating volumes, we investigated the effect of cutoff values on simulations of clean molten salts. We found that cutoff values had a dramatic effect on simulated density. Accordingly, we increased these cutoffs until doing so no longer had an effect on average density. Figure 6-2 illustrates this process for FLiNaK at 940K and shows an interesting result:
the density value that the simulation converges on as energy cutoff is raised is almost exactly the experimentally-measured density as found in the literature. This suggests that relatively small errors in energy calculation can lead to significant errors in the prediction of actual macroscopic properties. (It should be noted that FLiBe did not converge precisely on experimentally-measured density; FLiBe density will be discussed further in the results section below).

Figure 9-8 shows the density distributions of two FLiNaK cells, both at 940K. The planewave cutoff of set 1 was 1600 Rydbergs while the cutoff of set 2 was 2000 Rydbergs. This 25% increase in cutoff resulted in a 4.5% decrease in the computed density. Further increasing the cutoff values beyond these limits does not seem to markedly increase accuracy as shown in Figure 9-9. In Figure 9-9 two FLiNaK cells at 1100K are compared. The first simulation, using set 1, used a planewave cutoff of 2000 Rydbergs, while the simulation using set 2 used a planewave cutoff of 3000 Rydbergs. The change in average density resulting from this 50% increase in cutoff value is a mere 0.077%, which is smaller than the error margins of this work.

This process led to a choice of 2000 Ry for the plane-wave cutoff and 120 Ry for the relative cutoff for all salt systems.

We also examined the impact of correcting for van derWaals (VdW) dispersion interactions. General DFT is incapable of describing these interactions, and they must therefore be specifically included; however, when we incorporated VdW dispersion forces in a simulation of FLiNaK and raised the energy cutoff to 2000 Ry with a relative cutoff of 120 Ry, we found that the simulation converged on a density significantly below experimental values. The corrections
Figure 9-8. Overlaid simulation density distributions comparing the effects of planewave cutoff values sets. The average density with its 95% confidence interval is also shown for each distribution.

Figure 9-9. Overlaid simulation density distributions comparing the impact of the planewave cutoff value sets used in this work versus much higher cutoffs. The average density with its 95% confidence interval is also shown for each distribution.
did reduce fluctuation of the cell volume; both effects can be seen in Figure 9-10. Including VdW corrections for FLiBe, on the other hand, led to densities somewhat closer to experiment, but still significantly off.

![Figure 9-10. The equilibration densities of two FLiNaK cells at 940K are shown, comparing the impact of including VdW corrections. An experimental correlation value is shown as well for reference.](image)

This presented to something of a conundrum. Before VdW methods were developed in the first place DFT using general gradient approximation was known to successfully describe many strongly interacting systems\(^{219}\), and molten salts certainly are strongly interacting, dominated by large ionic energies. It is also puzzling that dispersion forces would lower density, as they are generally long-range attractive forces and would be expected to increase it. Previous AIMD studies of FLiBe\(^ {98}\) and KLiCl\(^ {54}\) found dispersion corrections to have the expected effect,
decreasing equilibrium volume. However, these studies used the projected augmented wave method (PAW) rather than GPW and the NVT ensemble rather than the NPT ensemble.

It may be that FLiBe is simply more sensitive to dispersion forces than FLiNaK, though in that case it is still troubling that including them made FLiNaK densities less accurate. One possibility would be to model FLiBe with VdW corrections and FLiNaK and KLiCl without, but that would mandate further justification.

With that in mind, we decided to neglect VdW corrections for the bulk of this study. However, future work will focus on exploring the effects of VdW correction in depth and confirming that the success of the methods used here in predicting FLiNaK density is not arbitrary.

9.5.2 Molybdenum in FLiNaK

While not discussed in the published results, an interesting conclusion of note occurred in the simulation of MoF$_3$ and H$_2$O in FLiNaK at 940K. The formation of a molecule of H$_2$ is observed in the final picosecond of simulation time. The constituents of the molecule are a H$^+$ ion previously solvated by two F$^-$ ions and a H$^-$ ion that was previously attached to the fluoro-oxo-molybdenum complex shown in Figure 9-6b. The Bader charge of this H$_2$ molecule is 0.0049. This process is not well understood, and merits additional investigation. However the formation of H$_2$ in molten fluorides has been observed in both FLiNaK and FLiBe$^{220}$.

9.5.3 Molybdenum in FLiBe

The mechanism of MoF$_3$ disproportionation may change over the temperature range of 500°C to 700°C. The composition of the molybdenum vapour product over FLiBe containing
MoF₃ is a function of the temperature. At 500°C, MoF₅ dominates the composition of the vapour phase, but at temperatures above 590°C MoF₄ begins to dominate¹⁹¹,¹⁹³. MoF₆ is observed in minute quantities over a range of temperatures¹⁹³. This shift in vapour product composition may be due to a change in MoF₃ disproportionation mechanism, or the relative solubilities of the vapour products as functions of temperatures, or proposed additional disproportionation reactions of MoF₄ and MoF₅. A definitive elimination of any of these possibilities is outside the scope of this work. However, if the dinuclear complexes found via AIMD simulation exhibit an existential dependence on temperature which closely correlates to the temperature dependence of the vapor composition, the first possibility may merit additional investigation.

FLiBe simulation cells containing only molybdenum fluoride additives spanned the temperature range of 500-723°C. Polynuclears were observed throughout the temperature range.

**Mononuclears**

Mononuclears were observed in FLiBe as MoF₆³⁻ and MoF₆²⁻. The mononuclears observed in FLiBe are structurally comparable to those observed in FLiNaK under comparable conditions. The coordination number for each monomer formed is 6, and the shape is octahedral. While no monomer formed for the simulation cell at the lowest temperature, this was likely impacted by the Mo count of 2 in that simulation cell, which formed a dinuclear. Based on the findings in FLiBe and FLiNaK, it is suspected that MoF₆ complexes are still observable at 500°C.
Figure 9-11. MoF$_6^{-}$ in FLiBe at 727$^\circ$C. The complex Bader charge is -2.38. This cell contained 66 F atoms, 28 Li atoms, 14 Be atoms, and 3 Mo atoms.

**Dinuclear molybdenum fluoride complexes** were readily found across the temperature range. The most common of these dinuclears consist of two centrally bonded molybdenums, each surrounded by a planar ring of fluorides, as shown in Figure 9-12 below. This structure was also readily observed in FLiNaK.

Weaver et al. found that the rate of disproportionation of Mo(III) into Mo(0) and Mo(IV), Mo(V) and Mo(VI) occurs independent of the surface area of the container, or the presence of plausible alternative solutes$^{189,192}$. This dinuclear is formed as two MoF$_6^{3-}$ mononuclear
complexes begin to share a fluoride in their first coordination shells, as shown in Figure 9-13 below.

Figure 9-12. Mo2F8- complex in FLiBe at 500°C. The complex Bader charge is -1.91. This cell contained 62 F atoms, 14 Be atoms, 28 Li atoms, and 2 Mo atoms.

Once this fluoride coordination shell overlap occurs, the two Mo$^{3+}$ ions coordinate, three additional fluoride ions are unbound and diffuse from the complex, leaving a dinuclear complex. The earliest version of the structure shown in Figure 9-13 observed in an equilibrated cell already included a shared fluoride.

One additional dinuclear was observed at 727°C, but at no lower temperature. It was only observed in a single simulation cell and is shown in Figure 9-14. This polymeric octahedral structure was also observed once in a FLiNaK cell, however both the oxidation state and the
Bader charge of the FLiNaK solvated complex varied significantly from this structure. While both were observed above 590°C, the transition temperature for the vapour composition above Figure 9-13. The mechanism of dinuclear formation involves two molybdenum hexafluoride mononuclears sharing a coordination fluoride ion.

FLiBe\textsuperscript{193}, they have not yet been observed below 590°C. However, no quantitative conclusions about the relative abundance of each species can be drawn from this small of a sample, therefore no definitive claims can be made about the nature of the disproportionation reactions intermediates from these data.

**Trinuclear**

Only one trinuclear complex was observed in FLiBe, and it occurred in the simulation cell at 667°C. More aptly, this is an overlap of fluoride solvation shell between a dinuclear and a mononuclear, and not a polymeric octahedra complex.
The average charge of all fluorides in complexation is \(-0.684\), while the average charge of all fluorides in solution is \(-0.845\). There is no statistical significance between the Bader charges of the fluorides predominantly in the monomer portion and those in the dimer portion.

Figure 9-14. Mo\(_2\)F\(_{10}\) complex formed in FLiBe simulation cell at 727°C. The complex Bader charge is \(-3.56\). This cell contained 66 F atoms, 28 Li atoms, 14 Be atoms, and 3 Mo atoms.

Figure 9-15. Molybdenum fluoride trinuclear complex observed in FLiBe at 667°C. The complex Bader charge is \(-2.95\). This cell contains 66 F atoms, 14 Be atoms, 28 Li atoms, and 3 Mo atoms.
The first-peak radii for the Mo-F pair RDFs for the mononuclear molybdenum ion is 1.953 Å and for the dinuclear molybdenum ions the first-peak radii is 1.951 Å. It is possible that this compound may be another intermediate in the disproportionation reaction. If this complex were to encounter a second dinuclear, the disproportion ratios noted by Senderoff and Mellors and Weaver et al. would be satisfied\textsuperscript{185, 186, 191, 195}.

*Uranium tetrafluoride impacts*

UF\textsubscript{4} at low concentrations does not affect disproportionation of MoF\textsubscript{3} in FLiBe\textsuperscript{193}. As with the FLiNaK simulation containing molybdenum and uranium additions, no visible impact on the formation of Mo\textsubscript{2}F\textsubscript{8}\textsuperscript{2-}.

One simulation included UF\textsubscript{4} additions to investigate impacts of U(IV) solutes on molybdenum dimerization. There was no clear impact on the dimerization of molybdenum under these conditions. Both a molybdenum monomer and a molybdenum dimer were observed.

This is in agreement with the findings of the Molten Salt Reactor Experiment (MSRE), which concluded that the molybdenum disproportion reaction was homogenous because its reaction rate was independent of, among other factors, the presence of UF\textsubscript{4}\textsuperscript{189, 192, 193}.

The mononuclear and both dinuclear complexes seen in FLiBe simulation cells were structurally observed in FLiNaK as well. This may suggest that the mechanism for disproportion of MoF\textsubscript{3} is the same in both salts. If this is the case, both the disproportionation mechanisms and the molybdenum complexes formed may have some transferability among fluoride salts of comparable ionic conditions.
Figure 9-16. Molybdenum fluoride and uranium fluoride complexes observed in FLiBe at 727°C. The complex Bader charge on the dinuclear is -1.99 and on the mononuclear is -1.71. This cell contained 14 Be atoms, 78 F atoms, 28 Li atoms, 3 Mo atoms, and 3 U atoms.

9.5.4 **Molybdenum in KLiCl**

While KLiCl is not the focus of this work, it is worth discussing briefly. This will yield some insight to the transferability of observations of molybdenum complexes between fluoride and chloride salts.

Senderoff and Mellors originally proposed a dinuclear molybdenum chloride complex as a product of a competing reaction of mononuclears\textsuperscript{195}. Curiously, ensuing studies have not
definitively found molybdenum chloride dinuclears in high temperature chloride molten salts\textsuperscript{187, 188, 197-199, 221-224}. However it has been suggested that an unidentified cathodic peak might correspond to an unknown Mo(III) compound in solution\textsuperscript{187, 199}. Molybdenum chloride dinuclears in ionic substrates have been found in room temperature ionic liquids\textsuperscript{225} and solids\textsuperscript{226, 227}.

We simulated two cells containing molybdenum chloride in KLiCl at 500°C. Each cell contained 56 Cl atoms, 28 K atoms, 22 Li atoms, and 2 Mo atoms.

Two structures formed in the first cell during the production run. The first observed structure is similar to the dinuclear found readily in FLiNaK and FLiBe. A reconfiguration of the complex without fluoride ion exchange occurred near the end of the production run. The restructure increases the Cl coordination number of the molybdenum ions from four to five, as shown in Figure 9-20. Fluctuations in the potential energy of the cell during this restructuring
amounted to less than 0.01% of the total cell energy, therefore no conclusions are drawn with respect to the relative energetic favorability of each configuration.

A third unique structure occurred in KLiCl. This polymeric structure is known to form with MoCl₄²⁻, and we saw a similar structure in FLiNaK with the addition of MoF₄. The Bader charges of the molybdenum complexes in both simulations cells are less negative compared to their fluoride counterparts at comparable conditions and oxidation states. This is likely due to the higher electronegativity and smaller ionic radii of fluoride in comparison to chloride ions, and the additional charge is likely delocalized on the solvating cation shell.

The structures depicted in Figure 9-18 and Figure 9-21 are quite similar to those already observed in FLiNaK and FLiBe. The charges more closely match the comparable structures observed in FLiBe simulations, but the resemblance to the FLiNaK complexes cannot be ignored. No mononuclear complexes have been observed yet, but this can be attributed to the formation of dinuclears in both KLiCl cells containing molybdenum, as each cell contained only 2 Mo atoms.

Figure 9-18. Mo₂Cl₈²⁻ complex found in KLiCl at 500°C
Figure 9-19. A second Mo2Cl82- complex found in the same simulation cell as Figure 9-18. The chloride coordination around each molybdenum ion has increased by one in this restructure. The complex Bader charge is -1.867.

Figure 9-20. The RDFs for the Mo-Cl pair before and after the restructuring of the complex.

It is possible that an alternative dinuclear molybdenum complex to that proposed by Senderoff and Mellors forms in molten KLiCl salts. While only a small sample of the state space for molybdenum complexation is sampled in these two simulation cells, it is significant that no
mononuclear complexes were formed. This would seem to indicate that these dinuclear complexes are allowed configurations, if not probable.
ON THE ELECTROCHEMICAL THERMODYNAMICS OF MINOR COMPONENTS IN MOLTEN SALT MIXTURES

As previously noted, the major advantage of molten salt solvation of fission products is the opportunity for continuous electrochemical separation, which requires thermodynamical information on the molten salt minor components. Due to the unique behavior of molten salts, identifying a suitable reference state is non-trivial. The following work by Fitzhugh et al. addresses this issue\(^4\). This work, comprising the remaining duration of Section 10, was co-authored with the author of this dissertation\(^4\). While much of the published work focuses on experimental electrochemistry\(^4\), the majority of the work is reproduced here. A key requirement of this dissertation is demonstrating that experimental behavioral predictions can be made from qualitative observations of phenomena in AIMD (see Section 1 of this work), and the mutual support of the experimental and computational veins of research is well demonstrated in the published work by Fitzhugh et al\(^4\). This collaborative work also further demonstrates the compatibility of AIMD simulation results with experimental analysis of molten salt chemistry\(^4\).

10.1 Introduction to the Electrochemical Thermodynamics of Minor Components in Molten Salt Mixtures

Molten salt mixtures have important applications in, for example, industrial metallurgical processes, energy storage for solar plants, and the development of advanced nuclear reactor
systems. Several unanswered questions in these systems involve the thermodynamics of minor components in the molten salt solution. Consequently, we examine molten salt systems using electrochemical thermodynamics, published experimental data, and atomistic simulations to accurately characterize interactions between a minor component and the base salt for multiple salts. The utility of an infinite dilution reference state is demonstrated and used to characterize the range over which solute-solvent interactions dominate over solute-solute interactions for minor components. Under such conditions, the activity is readily defined and cell potential can be easily determined as a function of concentration with use of an appropriate standard potential. Experimental data show that reactions can proceed at very different potentials in different salt melts, and molecular dynamics simulations are used to quantify differences between salts. Simulations show that the chemical potential of an anion varies between melts as influenced by the different cations present in each melt. Hence, attempts to use a common reference reaction for different salt mixtures are at best an approximation. Simulations also demonstrate that solute-solute interactions become significant at lower concentrations if the minor component includes an anion that is different from that of the base salt. This work helps to enhance our understanding of the behavior of minor components in molten salts, which is important for the development of future energy technologies.

Molten salt mixtures have been used in industrial metallurgical processes\textsuperscript{229}, energy storage for solar plants\textsuperscript{230}, and the development of advanced nuclear reactor systems\textsuperscript{175}. Several major unanswered questions in these systems involve the thermodynamics of minor components in the molten salt solution. This is particularly true for corrosion\textsuperscript{231} and for chemical processing systems to enable cleanup and recycle of the fuel salt in a molten salt reactor\textsuperscript{131}. 
Recent molten salt literature shows a lack of standardization in certain thermodynamic conventions, especially regarding standard states for activity, as has been noted elsewhere. While the choice of standard state is not unique as long as it is paired with the appropriate activity corrections, use of different standard states makes it difficult to compare and use data from a variety of sources. Furthermore, the choice of standard state impacts the quantity and type of data needed in order to characterize the system, as well as the utility of simplifying assumptions. Finally, the standard state also impacts the level of physical insight available from the data.

Because of the importance of minor components in corrosion and chemical separations, the present paper examines the choice of standard state for components known to be present in dilute concentrations in a molten salt mixture.

10.2 The Importance of the Standard State in Defining Activity Coefficients

There are two common standard states advocated in the literature for minor components in molten salts. The first uses the pure-component properties of the minor component in the liquid state as the standard. For example, the standard state for nickel ions in a LiCl-KCl melt would be liquid NiCl₂. The second standard state is referenced to the minor component at infinite dilution in the salt mixture of interest. This standard only considers interactions between the minor component and the base salt. It is the most commonly used standard for electrochemical systems in general, but its use has been limited in molten salt systems. Both standard states are considered at the temperature of interest and are illustrated qualitatively in Figure 10-1. Note that the infinitely dilute standard much more closely approximates the actual situation for a minor
component in a molten salt. Hence, activity coefficient corrections are expected to be much less significant when working from this standard.

Figure 10-1. Illustration of standard states for minor components in molten salt systems.

We will now examine the implications of using these standard states to analyze an electrochemical cell with a molten salt electrolyte. Consider a cell at open circuit consisting of a silver/silver chloride reference electrode and a cobalt/cobalt chloride working electrode, both of which are immersed in the same NaCl-KCl melt (see Figure 10-2). This system was analyzed by Hamby, who collected data for several concentrations of cobalt chloride. The full dataset will
be shown later. The procedure used for analysis is that of Newman and Thomas, applicable to a cell at equilibrium\textsuperscript{234}. The cell can be described as follows:

\begin{center}
\begin{tabular}{c|c|c|c|c}
\hline
\(\alpha'\) & \(\beta'\) & \(\beta\) & \(\alpha\) \\
Ag(s) & AgCl in NaCl-KCl & CoCl\textsubscript{2} in NaCl-KCl & Co(s) \\
\hline
\end{tabular}
\end{center}

where the \(\alpha\), \(\beta\), \(\alpha'\), and \(\beta'\) refer to distinct chemical phases. The half-cell reactions that correspond to this cell are:
\[ Co^{2+} + 2e^- \leftrightarrow Co \]  
\[ Ag^+ + e^- \leftrightarrow Ag \]  
(10-1)  
(10-2)

Since the cell is at open circuit, these half-reactions are each in equilibrium. The next equations describe phase equilibrium for each half reaction:

\[ \mu^α_{Co(s)} = \mu^β_{Co^{2+}} + 2\mu^α_{e^-} \]  
(10-3)  
\[ \mu^α_{Ag(s)} = \mu^β_{Ag^+} + \mu^α_{e^-} \]  
(10-4)

In the above equations, \( \mu_i \) refers to the electrochemical potential of species \( i \). The electrochemical potential of the ions and metals are easily defined with the equations of chemical thermodynamics. The electrochemical potential of the electrons, like that of the ions, is dependent on the electric potential. For electrons, it is defined as:

\[ \mu_{e^-} = zF\Phi = -F\Phi \]  
(10-5)

In the equation above, \( F \) is Faraday’s constant, \( z \) is the charge number (which for an electron is \(-1\)), and \( \Phi \) is the electric potential. We can now define the cell potential in terms of the difference in potential of the electrons in the two electrodes:

\[ E = (\Phi^α - \Phi^α') = \frac{(\mu^α_{e^-} - \mu^α_{e^-})}{F} \]  
(10-6)

where \( E \) is the cell potential. Next we use equations 10-3 and 10-4 to get the electrochemical potentials of the electrons in terms of the electrochemical potentials of the chemical components to yield:
\[
F(\Phi^\alpha - \Phi^\alpha_\text{eq}) = FE = \left(\mu_e^{\alpha'} - \mu_e^{\alpha}\right) = \mu_{A_g(s)}^{\alpha'} - \mu_{A_g^+}^{\alpha'} - \frac{1}{2} \mu_{C_{o(s)}}^{\alpha'} + \frac{1}{2} \mu_{C_{o^2+}}^{\beta}
\]

Now we introduce the activity, which is a thermodynamic quantity that corrects the electrochemical potential in a specified reference state to the actual conditions in solution. It is defined as follows:\(^{235}:\)

\[
\mu_i = \mu_i^0 + RT \ln a_i
\]  
(10-8)

In the above equation, \(a_i\) is the activity of species \(i\), \(\mu_i^0\) is the electrochemical potential of species \(i\) in its standard state, \(\mu_i\) is the electrochemical potential of species \(i\) as indicated previously, \(R\) is the Universal Gas Constant, and \(T\) is the temperature. We note that pure metals are in their standard state and need no activity correction. By substituting Equations 10-7 into Equation 10-6 for each occurrence of the electrochemical potential, the following is obtained:

\[
FE = \mu_{A_g(s)}^0 - \mu_{A_g^+}^0 - \frac{1}{2} \mu_{C_{o(s)}}^0 + \frac{1}{2} \mu_{C_{o^2+}}^0 + \frac{RT}{2} \ln a_{C_{o^2+}} - RT \ln a_{A_g^+}
\]  
(10-9)

Note that we have not yet defined the reference state used in defining the activity, and that the above was done with no loss of generality, except that we have assumed that the cobalt and silver ions are dissociated in the melt. Next we introduce the standard potential for the cell reaction, denoted \(E^0\), with the following definition:

\[
E^0 = \frac{\mu_{A_g(s)}^0 - \mu_{A_g^+}^0 - \frac{1}{2} \mu_{C_{o(s)}}^0 + \frac{1}{2} \mu_{C_{o^2+}}^0}{F}
\]  
(10-10)

The standard potential is the potential of the cell, not of an electrode or a specific component, where all of the reactants and products are in their standard state. Dividing Equation
10-9 by F and substituting in the standard potential defined in Equation 10-10, we obtain a substantially simplified equation:

\[ E = E^0 + \frac{RT}{2F} \ln a_{Co^{2+}} - \frac{RT}{F} \ln a_{Ag^+} \]  

(10-11)

Activity of ions in molten salt mixtures is usually represented as the product of the activity coefficient and the concentration:

\[ a_i = m_i \gamma_i \]  

(10-12)

In this equation, \( m_i \) is the molality of component \( i \). Also, \( \gamma_i \) is the activity coefficient, which is essentially a correction to the molality to give the correct activity value at the composition of interest. Different concentration scales can be used to express the activity; the choice of molality is motivated by the fact that it avoids ambiguity and is not a function of temperature. Substituting Equation 10-12 into Equation 10-11 we obtain:

\[ E = E^0 + \frac{RT}{2F} \ln m_{Co^{2+}} - \frac{RT}{F} \ln m_{Ag^+} + \frac{RT}{2F} \ln \gamma_{Co^{2+}} - \frac{RT}{F} \ln \gamma_{Ag^+} \]  

(10-13)

Neutral combinations of activity coefficients are typically measured experimentally for a wide variety of systems. Although single-ion activity coefficients are generally considered problematic, the expression in Equation 10-13 is useful for minor components in molten salts as will be explained further below.

10.3 The Standard State from Infinite Dilution for Minor Components

At this point we address the standard state of the components. As mentioned above, two principal standard states are used for components that are not main constituents of the salt: pure component and infinite dilution. “Infinite dilution” means infinitely dilute in the melt being considered. The key concept behind the infinitely dilute standard state is that the minor
component is so dilute that the only interactions are between the solute (minor component or impurity) and the solvent (in this case, the base molten salt). In other words, at the standard state there are no solute-solute interactions. It follows from this definition that the activity coefficient is equal to one at low concentrations where the “infinite dilution” condition is closely approximated. Under such conditions for the cell shown in Figure 10-2 and described in Equation 10-13, the term containing the activity coefficient is equal to zero for cobalt and the measured potential varies linearly with the logarithm of its molality, assuming that conditions within the reference electrode remain constant, which is a fundamental characteristic of a reference electrode. Under such conditions, Equation 10-13 can be rewritten as a line:

$$E_{Cell} = E_{int} + \frac{RT}{2F} \ln m_{Co^{2+}}$$  \hspace{1cm} (10-14)

where $E_{Cell}$ is the measured cell potential and $E_{int}$ is the intercept potential, defined below. If a plot of measured potential vs log concentration is linear and if the theoretical slope fits the data well, it is an indication that the concentrations were measured in a sufficiently dilute range and that the half-cell reaction was accurate as written. This line can then be extrapolated to the point of unit concentration, where the concentration term in Equation 16 is equal to zero, to obtain the intercept, which we call $E_{int}$. $E_{int}$ includes the standard potential and a contribution from the reference electrode as follows:

$$E_{int} = E^0 - \frac{RT}{F} \ln m_{Ag^+} - \frac{RT}{F} \ln \gamma_{Ag^+}$$  \hspace{1cm} (10-15)

The infinite dilution reference state has been used in the literature\textsuperscript{236-242}, and is illustrated in Figure 10-3 using data for CoCl\textsubscript{2} in NaCl-KCl measured by Hamby\textsuperscript{233}. While the data were originally measured on a mole fraction scale, they have been converted to molality. They are also plotted using log\textsubscript{10} instead of natural logs to give greater ease in reading the plots; the same
convention is followed throughout this work. A line with the theoretical slope of 0.1064 V mol\(^{-1}\) (using log\(_{10}\)) is an excellent fit through the data at low concentrations. The measured potential at unit molality (\(E_{\text{int}}\)) is \(-1.258\) V, which is the intercept of the line. The actual reference state for the standard potential is not a 1 molal solution, but a hypothetical 1 molal solution where only interactions between the solute and the base salt are important. This hypothetical reference state is obtained by extrapolating the line through the low-concentration data to unit molality. In general, the actual data at a one molal solute concentration will not fall on this line since solute-solute interactions are likely to have some effect at that concentration. For this particular case, this can be seen as the difference between the potential that corresponds to the line at unit molality and that which corresponds to the curve that passes through the actual data at the same concentration. This difference can be large or small, and depends on the system and the concentration units used.

Figure 10-3. Infinite dilution linear fit on molality scale for CoCl\(_2\) in NaCl-KCl at 1073 K. Data from Hamby\(^{233}\) fit to the theoretical slope of 2.303RT/nF rather than linear regression.
The linear change in the potential with the logarithm of the cobalt chloride concentration (equivalent to the concentration of cobalt ions) is different than the classical nonlinear behavior expected if the same salt were added to pure water\textsuperscript{243}. Specifically, if CoCl$_2$ were added to water, we would expect the activity, and hence the potential, to scale with $\ln (m_{\text{CoCl}_2})$ at low concentrations since each molecule of salt will dissociate into three ions. In contrast, when CoCl$_2$ is added to a molten chloride salt, the small amount of chloride added does not impact the activity of Cl$^-$ in the melt and the potential scales linearly with the log of the cation concentration. This will be true for the addition of solute salts that have a common anion with the base molten salt, and justifies the use of the single-ion activity coefficient of Co$^{2+}$.

If, therefore, we match the infinite-dilution standard state to a CoCl$_2$ concentration of (in this case) one molal or less, we can ignore the activity coefficient with a small error in our cell potential, which we quantify for this system below, leading to the following equation for the overall cell potential:

$$E = E^0 + \frac{RT}{2F} \ln m_{\text{Co}^{2+}} - \frac{RT}{F} \ln m_{\text{Ag}^+} + \frac{RT}{F} \ln \gamma_{\text{Ag}^+} = E_{\text{Int}} + \frac{RT}{2F} \ln m_{\text{Co}^{2+}}$$ (10-16)

In order to obtain the true standard potential rather than the intercept potential, one needs additional data for the reference electrode in the salt melt of interest. Such data were obtained for the silver/silver chloride reference electrode in NaCl-KCl by Flengas et al., who showed that the activity coefficient was not significant up to a silver chloride mole fraction $x_{\text{AgCl}} = 6.103 \times 10^{-2}$.\textsuperscript{244} While Hamby’s reference electrode used a concentration of $x_{\text{AgCl}} = 6.6 \times 10^{-2}$, this is close to the range defined by Flengas et al. and any error incurred by neglecting the activity coefficient of Ag$^+$ is not likely to be significant. Therefore, converting the mole fraction to molality using a molar mass of 1:1 NaCl-KCl eutectic of 66.496 g mol$^{-1}$, we obtain a AgCl molality of approximately 1.06 and a potential correction of about 6 millivolts, leading to a final standard
potential of −1.264 V for Co/CoCl₂ vs Ag/AgCl in NaCl-KCl at 1073 K. In this case one can use the standard potential and concentration of Co²⁺ and Ag⁺, constrained to the infinitely dilute region, to calculate the potential of this cell at 1073 K as follows:

$$E = E^0 + \frac{RT}{2F} \ln m_{Co^{2+}} - \frac{RT}{F} \ln m_{Ag^+}$$  \hspace{1cm} (10-17)

The linear behavior for the Co/Co₂⁺ system considered above extends nearly to unit molality (see Figure 10-3), which is greater than 1 mol\% of the minor component in the mixture as shown in greater detail below. Thus, the cell potential can be determined assuming an activity coefficient of unity without appreciable error for a relatively wide composition range of a minor component when using the infinite dilution standard state.

### 10.4 Comparison of Infinite Dilution and Pure Component Standard States

Since the potential actually measured must clearly be independent of the standard state chosen, we will now compare the activities from the infinite dilution standard state to those from the pure solute liquid standard. In order to facilitate this comparison, we will switch the concentration scale to mole fraction. On the mole fraction scale, the standard potential from infinite dilution and that from the pure component reference both correspond to unit mole fraction. While the concept of extrapolating an infinitely dilute solution to a mole fraction of unity is difficult to grasp physically (it essentially postulates a pure component that “acts like” it is infinitely dilute in the relevant salt melt), it is easy mathematically and provides a good basis for comparison. In this work, the mole fraction is taken as the ratio of moles of cations of the species of interest to total moles of cations, or equivalently, moles of the species of interest to total moles of neutral salt.
Table 10-1. Measured data from Hamby for potential of CoCl$_2$ at 1073 K$^{233}$.

<table>
<thead>
<tr>
<th>Mole Fraction CoCl$_2$</th>
<th>Measured Potential (V)</th>
<th>Activity Coefficient (Pure Component Reference)</th>
<th>Activity Coefficient (Infinite Dilution Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>1.45</td>
<td>$3.41 \times 10^{-3}$</td>
<td>$9.84 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.003</td>
<td>1.39</td>
<td>$3.50 \times 10^{-3}$</td>
<td>$1.01 \times 10^{0}$</td>
</tr>
<tr>
<td>0.007</td>
<td>1.35</td>
<td>$3.49 \times 10^{-3}$</td>
<td>$1.01 \times 10^{0}$</td>
</tr>
<tr>
<td>0.020</td>
<td>1.31</td>
<td>$3.45 \times 10^{-3}$</td>
<td>$9.95 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.050</td>
<td>1.26</td>
<td>$3.98 \times 10^{-3}$</td>
<td>$1.15 \times 10^{0}$</td>
</tr>
<tr>
<td>0.070</td>
<td>1.24</td>
<td>$4.68 \times 10^{-3}$</td>
<td>$1.35 \times 10^{0}$</td>
</tr>
<tr>
<td>0.10</td>
<td>1.21</td>
<td>$5.87 \times 10^{-3}$</td>
<td>$1.69 \times 10^{0}$</td>
</tr>
<tr>
<td>0.15</td>
<td>1.17</td>
<td>$8.52 \times 10^{-3}$</td>
<td>$2.46 \times 10^{0}$</td>
</tr>
<tr>
<td>0.20</td>
<td>1.14</td>
<td>$1.33 \times 10^{-2}$</td>
<td>$3.85 \times 10^{0}$</td>
</tr>
<tr>
<td>0.25</td>
<td>1.10</td>
<td>$2.18 \times 10^{-2}$</td>
<td>$6.29 \times 10^{0}$</td>
</tr>
<tr>
<td>0.30</td>
<td>1.07</td>
<td>$3.87 \times 10^{-2}$</td>
<td>$1.12 \times 10^{1}$</td>
</tr>
<tr>
<td>0.35</td>
<td>1.04</td>
<td>$6.77 \times 10^{-2}$</td>
<td>$1.95 \times 10^{1}$</td>
</tr>
<tr>
<td>0.40</td>
<td>1.01</td>
<td>$1.13 \times 10^{-1}$</td>
<td>$3.27 \times 10^{1}$</td>
</tr>
<tr>
<td>0.50</td>
<td>0.948</td>
<td>$3.25 \times 10^{-1}$</td>
<td>$9.38 \times 10^{1}$</td>
</tr>
<tr>
<td>0.70</td>
<td>0.890</td>
<td>$8.14 \times 10^{-1}$</td>
<td>$2.35 \times 10^{2}$</td>
</tr>
<tr>
<td>0.90</td>
<td>0.868</td>
<td>$1.02 \times 10^{0}$</td>
<td>$2.94 \times 10^{2}$</td>
</tr>
<tr>
<td>1.00</td>
<td>0.864</td>
<td>$1.00 \times 10^{0}$</td>
<td>$2.89 \times 10^{2}$</td>
</tr>
</tbody>
</table>

Figure 10-4. Infinite dilution linear fit on mole fraction scale for CoCl$_2$ in NaCl-KCl at 1073 K, compared to pure component standard potential for the same data. Data from Hamby$^{233}$ fit to the theoretical slope of 2.303RT/nF.
By definition, the activity is unity at the standard state. Since the mole fraction is also equal to one at the standard state as defined above, the activity coefficients must also equal one. Therefore, we expect activity coefficients to be close to unity as the concentration of cobalt chloride gets smaller when using the infinite dilution standard. In contrast, we expect the opposite for the pure component reference state. This is exactly what is observed for the measured data as shown in Table 10-1, Figure 10-4, and Figure 10-5, analyzed using both standard states.

Figure 10-5. Comparison of the activity coefficients calculated for CoCl₂ in NaCl-KCl by two different methods: (a) concentration on mole fraction scale, and (b) concentration on molality scale. The relationship between the concentration and the activity is shown in (b) for both standard states.

The table and figures also show the consequences of assuming either of these particular standard states and calculating the activity coefficients on that basis. Both lines in Figure 10-4 make use of Equation 10-13 with the concentration of silver held constant and cobalt activity coefficient equal to one. The infinite dilution standard potential was obtained by extrapolating from the first four points of the data set in Table 10-1 as explained above. As may be seen from
the table, the activity correction is minimal when using the infinite dilution standard state at a CoCl₂ concentration of 10% or less, and large when the CoCl₂ concentration is above 70%. These data are consistent with the situation shown qualitatively in Figure 10-1 and illustrate the appropriateness of the infinite dilution reference state for minor components in the salt. Figure 10-5 shows the activity coefficient values obtained by fitting Equation 10-13 to the data in Figure 10-4. With the infinite dilution standard state, the activity coefficients are equal to one at low concentrations as expected. Thus, one does not need the activity coefficient to accurately calculate the potential for low concentrations of the solute (<1 molal in this case). In contrast, although the activity coefficient reaches a constant value for the pure component standard state as expected for the present situation, the value of the activity coefficient is orders of magnitude below one and would need to be measured.

10.5 Implications of Infinite Dilution Standard States for the Activity of Cations

Either of the two standard states considered will yield the correct cell potential for reactions involving minor components if the correct activity coefficients are used. However, it appears that the infinite dilution standard state has some benefits when dealing with minor components.

The first major benefit was seen above; activity coefficients are essentially equal to one at low concentrations. This allows prediction of the potential with relatively little error in the dilute region without the need to measure the activity coefficient. For instance, at a mole fraction of about 2% for CoCl₂ in NaCl-KCl, the error incurred by ignoring the activity coefficient when estimating the potential of CoCl₂ is −0.257 V with a liquid pure-component standard state, and about 0.002 V when using the infinite dilution standard state. This method of analysis also
reduces the amount of data necessary to analyze the system. In a “worst case” scenario, one
could obtain an accurate estimate of the potential for the entire dilute region from a single data
point and the theoretical slope for the region in which the activity coefficient is equal to one.

A more important consideration than the amount of data required to perform calculations
is the physical insight available from the data. For example, an activity coefficient of one when
using the infinite dilution reference state is consistent with the physical situation where the major
interactions of the solute are with solvent ions. In contrast, solute-solute interactions have begun
to measurably impact the cell potential when the activity coefficient diverges from unity.

Another benefit of this approach is provided when performing a Pourbaix-style corrosion
analysis in molten-salt systems. There have been Ellingham-type diagrams published in the
recent literature of the standard potential of various components in molten fluorides at an activity
of $10^{-6}$. Use of a concentration of $10^{-6}$ M is standard for corrosion analysis in electrochemical
literature and is essentially equivalent to the activity as commonly used when activity is reported
on a molarity scale. Molarity is not a concentration scale commonly used in molten salts, and is
not convenient when working at high temperatures due to its dependence on the density of the
solvent, so we will use molality as a close proxy. There is a potential pitfall if an activity value is
assumed in molten salt systems without careful consideration of the standard state of the
component in question. Specifically, an activity of $10^{-6}$ doesn’t imply a concentration that is
particularly close to $10^{-6}$ on any concentration scale.

As we see from Figure 10-5b, when considering CoCl$_2$ in NaCl-KCl, an activity of $10^{-6}$
with a pure-component liquid standard state actually means a molality of $4.55 \times 10^{-3}$, something
that would not be obvious from considering a diagram that simply states that the activity is $10^{-6}$.
A reader attempting to use such a diagram may easily confuse activity with concentration and be
in error by several orders of magnitude if unaware of the fact that activity coefficients do not approach one at low concentrations for the pure-component standard state and that the activity coefficient at low concentrations varies among different chemical components and for different molten salts. When a standard state from infinite dilution is used, this pitfall is avoided because an activity of $10^{-6}$ clearly implies a molality of $10^{-6}$.

The reason for these benefits is that the infinite dilution standard state is closer to the actual state of the minor component in solution.

This reference state assumes the opposite of pure-component reference; namely, it assumes that the most important interactions experienced by the solute are with the solvent rather than with other solute ions.

10.6 Salt-Specific Effects

There are many examples in the literature where reactions in different melts have been compared by putting them on the same scale. This is usually done through the use of shared reaction, such as the $\mathrm{F}_2/\mathrm{F}^-$ reaction or $\mathrm{Cl}_2/\mathrm{Cl}^-$ reaction for fluoride and chloride melts, respectively. Use of a shared reaction for different salts is seemingly analogous to the standard hydrogen electrode that serves as the reference for aqueous systems. When examined closely, this turns out to be an imperfect analogy. To examine this, we will use electrochemical potentials as shown below in Equation 10-18, which is an alternate form of Equation 10-10:

$$\Delta G_{\text{Co/Ag}}^0 = -FE^0 = -\mu_{\text{Ag}(s)}^0 + \mu_{\text{Ag}^+}^0 + \frac{1}{2} \mu_{\text{Co}(s)}^0 - \frac{1}{2} \mu_{\text{Co}^{2+}}^0$$

(10-18)
A similar expression for the cobalt reaction in an aqueous system referred to a standard hydrogen electrode is:

\[
\Delta G_{\text{Co}/H_2}^0 = -\frac{1}{2} \mu_{H_2}^0 + \mu_{H^+}^0 + \frac{1}{2} \mu_{\text{Co}(s)}^0 - \frac{1}{2} \mu_{\text{Co}^{2+}}^0
\]  

(10-19)

Most aqueous data are reported at room temperature. According to standard practice, the chemical potential of H_2 at 25 °C is defined to be zero. The electrochemical potential of H^+ is likewise defined as zero for a hypothetical 1 molal solution at 25 °C using the common infinite dilution reference state. Importantly, the H^+ reference state is independent of the solute owing to the infinite dilution reference, and is thus the same for all aqueous systems. Equation 10-19 may now be written for aqueous systems as

\[
\Delta G_{\text{Co}/H_2}^0 = \frac{1}{2} \mu_{\text{Co}(s)}^0 - \frac{1}{2} \mu_{\text{Co}^{2+}}^0
\]  

(10-20)

Returning to Equation 10-18, an analogous procedure is not workable in molten salts. For example, for CoCl_2 in a chloride-based molten salt, the standard potential against a chlorine reference is:

\[
\Delta G_{\text{Co}/\text{Cl}_2}^0 = \frac{1}{2} \mu_{\text{Cl}_2}^0 - \mu_{\text{Cl}^-}^0 + \frac{1}{2} \mu_{\text{Co}(s)}^0 - \frac{1}{2} \mu_{\text{Co}^{2+}}^0
\]  

(10-21)

However, neither of the terms associated with the chlorine electrode are equal to zero. First, the Gibbs energy of formation of Cl_2, is by definition equal to zero at 25 °C, and therefore has a finite value at temperatures relevant to molten salts. Also, the electrochemical potential of the anion enters into the picture and is different for each salt melt, depending on the cations in the melt, since the cations present have a strong influence on how the anions coordinate. Therefore, the standard potential of the chloride ion cannot be defined independently from the salt for the infinite dilution reference or independently of the pure liquid solute for the pure
component reference, and its value cannot arbitrarily be set to zero. More data are presented below to confirm that the anion electrochemical potential cannot be taken as zero in Equation 10-21.

Table 10-2. Comparison of various reactions’ standard potentials compiled by Plambeck, standard potentials referenced to the molality scale. Many reactions’ standard potentials are extremely similar between the two melts but some are not; those that are not are marked in red and italicized.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Standard Potential LiCl-KCl</th>
<th>Standard Potential NaCl-KCl-MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)/Mg(0)</td>
<td>−2.58</td>
<td>−2.646</td>
</tr>
<tr>
<td>Al(III)/Al(0)</td>
<td>−1.762</td>
<td>−1.886</td>
</tr>
<tr>
<td>Zn(II)/Zn(0)</td>
<td>−1.566</td>
<td>−1.55</td>
</tr>
<tr>
<td>Cr(II)/Cr(0)</td>
<td>−1.425</td>
<td>−1.396</td>
</tr>
<tr>
<td>Cd(II)/Cd(0)</td>
<td>−1.316</td>
<td>−1.312</td>
</tr>
<tr>
<td>Fe(II)/Fe(0)</td>
<td>−1.172</td>
<td>−1.183</td>
</tr>
<tr>
<td>Pb(II)/Pb(0)</td>
<td>−1.101</td>
<td>−1.171</td>
</tr>
<tr>
<td>Sn(II)/Sn(0)</td>
<td>−1.082</td>
<td>−1.147</td>
</tr>
<tr>
<td>\textit{Cr(III)/Cr(0)}</td>
<td>\textbf{−0.65}</td>
<td>\textbf{−1.131}</td>
</tr>
<tr>
<td>Co(II)/Co(0)</td>
<td>−0.991</td>
<td>−0.97</td>
</tr>
<tr>
<td>Cu(I)/Cu(0)</td>
<td>−0.957</td>
<td>−0.947</td>
</tr>
<tr>
<td>\textit{Fe(III)/Fe(0)}</td>
<td>\textbf{−0.362}</td>
<td>\textbf{−0.852}</td>
</tr>
<tr>
<td>Ni(II)/Ni(0)</td>
<td>−0.795</td>
<td>−0.792</td>
</tr>
<tr>
<td>Ag(I)/Ag(0)</td>
<td>−0.743</td>
<td>−0.763</td>
</tr>
<tr>
<td>\textit{Sb(III)/Sb(0)}</td>
<td>\textbf{−0.635}</td>
<td>\textbf{−0.745}</td>
</tr>
<tr>
<td>Bi(III)/Bi(0)</td>
<td>−0.635</td>
<td>−0.626</td>
</tr>
<tr>
<td>Cu(II)/Cu(0)</td>
<td>−0.448</td>
<td>−0.519</td>
</tr>
<tr>
<td>\textit{Fe(III)/Fe(II)}</td>
<td>\textbf{0.086}</td>
<td>\textbf{−0.19}</td>
</tr>
<tr>
<td>\textit{Cu(II)/Cu(I)}</td>
<td>\textbf{0.061}</td>
<td>\textbf{−0.091}</td>
</tr>
</tbody>
</table>

The precise way in which the difference in electrochemical potential affects the standard potential will depend on the standard state used. However, independent of the standard state used, the electrochemical potential of the salt anion is different for each salt and there exists no molten-salt equivalent to a standard hydrogen electrode, as is sometimes implied in the literature. However, the differences may not be large for similar salts and a common scale might be useful.
in some cases; even then, it should be recognized as an approximation. In stating this, we remind the reader that the standard state must be at the temperature of the system.

Another challenge associated with these effects is that different solvent melts seem to affect certain cations much more than others. Jenkins\textsuperscript{245} provides a clear example of this. He gathered data on the Fe(III)/Fe(II), Fe(II)/Fe(0), and Ni(II)/Ni(0) redox couples in FLiBe and FLiNaK, using the infinite dilution standard state. These data showed that the standard potentials of the Ni(II)/Ni(0) couple and the Fe(II)/Fe(0) couple were similar for both solvents, within 25 mV of each other, while the standard potential of the Fe(III)/Fe(II) couple shifted drastically, by almost 0.4 V. Jenkins explained the observed behavior as due to greater stability of the Fe(III) ion in FLiNaK than in FLiBe, but did not propose a theoretical reason for the increase in stability\textsuperscript{245}. We also note that the same difference in potential in different salts does not guarantee that the absolute values of the potentials are the same in each salt.

The difficulty, in our view, of using any pure-component standard state for minor components in molten salts, is that all the effects just described would be bundled into the activity coefficient only. Thus, according to the data of Jenkins, neglecting the activity coefficient or trying to calculate reactions without reliable activity data could cause the calculated potential to be incorrect by 0.35 V or more. Further data supporting this idea are shown below.

\textbf{10.7 Data Supporting the Variation in Activity between Different Salt Melts}

\textbf{10.7.1 Experimental Data}

The effect of the salt on the standard potential may also be seen in data presented by Plambeck\textsuperscript{236} for LiCl-KCl and MgCl\textsubscript{2}-NaCl-KCl, shown in Table 10-2. These data were
referenced by Plambeck to the infinite dilution standard state with Pt(II)/Pt at infinite dilution set to 0 V. Since they are referenced to the same reaction in different melts, a comparison between them may serve to illustrate the error incurred by assuming that certain reactions will be at the same standard potential relative to a particular reference when both the half-reaction and the reference are considered independently of the salt melt. While the temperature at which the data were measured varied slightly, they are close enough to be comparable (773 K for LiCl-KCl series and 748 K for the MgCl2-NaCl-KCl series). Most of the potentials presented in both solvents on the molality scale are within a few hundredths of a volt in both salt melts, but a few reactions vary by more than 0.5 V between melts. All reactions that vary by more than 0.1 V are marked in red and italicized in the table. The larger variations are especially pronounced in the higher oxidation states of species exhibiting multiple oxidation states in the melt, which is in line with the observations of Jenkins noted previously and suggests that this effect is not simply due to experimental error.

Figure 10-6. Infinite dilution linear fit on mole fraction scale for the electrochemical cells in Hamby\textsuperscript{233} at 1073 K in various solvents. Data fit to the theoretical slope of 2.303RT/nF rather than linear regression. Left, (a) Co/Ag Cell. Right, (b) Ni/Ag Cell.
Table 10-3. Intercept Potentials ($E_{\text{int}}$ from Equation 10-15) from infinite dilution extrapolation for NiCl$_2$ and CoCl$_2$ in various solvents at 1073 K.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Nickel</th>
<th>Cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>−1.113</td>
<td>−1.320</td>
</tr>
<tr>
<td>NaCl—KCl</td>
<td>−1.081</td>
<td>−1.257</td>
</tr>
<tr>
<td>NaCl</td>
<td>−0.994</td>
<td>−1.192</td>
</tr>
<tr>
<td>LiCl</td>
<td>−0.890</td>
<td>−1.076</td>
</tr>
</tbody>
</table>

As a further illustration of the difference made by different solvents in the standard potential of a particular reaction, we summarize here the main dataset from Hamby at 1073 K$^{233}$ as shown in Figure 10-6a and b and Table 10-3. Because information is not available about the silver-silver chloride reference electrode in all of these melts, Table 10-3 compares the intercept potential as defined in Equation 10-15. It remains unclear whether the nickel/cobalt (solute) or silver (reference) potential was more affected by the change of solvents, but it is clear that different salt melts will produce different cell potentials. More experimental data on the silver-silver chloride reference electrode in all of these solvents would aid in determining if the reference or the solute is responsible for the bulk of the changes seen, but the differences in spacing between some of the lines between Figure 10-6a and b suggest that the solute reaction is responsible for at least some of the observed changes.

10.7.2 *Ab initio molecular dynamics (AIMD) simulations*

We have also performed molecular dynamics simulations to look at the behavior of various ions in salt melts. These simulations calculate detailed information about the electronic configurations of individual atoms that is not accessible by experiment and support the premise that an ion will have a different chemical potential in different molten salts. We explored the
distinct electronic behavior of one ion—in this case, the fluoride anion—as a function of its solvating environment by simulating two molten salts, FLiBe and FLiNaK, using ab initio molecular dynamics (AIMD) simulations. These AIMD simulations utilize Density Functional Theory (DFT), a numerical approximation of the electronic structure of a small system of condensed-phase atoms. The electron cloud of an ion can be approximated with use of its Bader volume\textsuperscript{104}, which is the portion of the total cell volume assigned to a specific ion. Each point in the electron density grid is assigned to a nucleus using a steepest-ascent partitioning scheme as detailed and implemented by the Henkleman group\textsuperscript{104}. Here we calculate the Bader volumes of the F$^-$ ions over the course of the AIMD simulations and show that their form depends strongly on the cations present in the melt. Changes in the average Bader volume are reflective of changes to the electron cloud of an ion. If the electron cloud of an anion is different in two distinct systems, then the anion’s contribution to the system’s total energy will also be different\textsuperscript{105}. Further, this change in the anion’s contribution to the total energy is related to the distinct impact of different ions surrounding the anion\textsuperscript{104}. The electron cloud of an anion is most notably compressed by solvating cations, as shown in Figure 10-7.

![Figure 10-7. Visual representation of the Bader volume of the F$^-$ ion in (a) FLiBe and (b) FLiNaK. The figures are on the same scale for ease of comparison. Brown: K$^+$; yellow: Be$^{2+}$; green: F$^-$; blue: Na$^+$; purple: Li$^+$.](image-url)
The compression of fluoride comes at a significant energy cost, but this can be offset if the solvating cation-anion interactions are sufficiently favorable\. Thus, a change in the Bader volume of fluoride from one salt to another represents a change in the interaction potentials between fluoride and the surrounding cations. The AIMD simulations utilized the AIMD simulation software package CP2K. Density functional theory (DFT) calculations utilized the Perdew-Burke-Ernzhof (PBE) exchange-correlation functional. Gaussian and plane-waves methods were employed to approximate the electron density and wavefunctions. All core electrons were treated with Goedecker-Teter-Hutter (GTH) pseudopotentials and all atoms were modeled using DZVP-MOLOPT-SR-GTH basis sets. Each simulation cell contains a fixed number of salt atoms randomly arranged via the PackMol software package, and was simulated under the NPT ensemble at 1 atm. The range of temperatures examined was 740–1000 K. All FLiBe simulations contained at least 93 ions and at most 98 ions, and all FLiNaK simulation cells contained at least 50 ions and at most 100 ions. Ion count and box size were not seen to affect the results of this study, and the charge for each cell was balanced. Each simulation was run to equilibration before running for an additional 10 ps of simulation time for analysis. The Bader volume of a \( \ce{F^-} \) ion is reported as the average of all fluoride ions in a simulation and over a simulation time of a few picoseconds. Bader volumes were computed using the Bader code as implemented by the Henkelman group. A more detailed explanation of our AIMD methodology is also given by Frandsen et al., as well as in Section 1 of this text and was found to accurately predict molten salt structure in this temperature range.
As seen in Figure 10-8, the Bader volume of a fluoride ion varies considerably between FLiBe and FLiNaK solutions. Figure 10-7 visually compares the Bader volumes of two fluoride ions, one in FLiBe and one in FLiNaK. In addition to a quantitative change to the Bader volume, a distortion of the anion’s shape is also observed. This distortion is most prominent along the surface of the Bader volume located between the F⁻ ion and its neighbouring Be²⁺ ion. In addition to coordinating closely to F⁻ ions, Be²⁺ ions are known to coordinate with F⁻ ions tetrahedrally⁹²; Figure 10-7 shows how this coordination dramatically affects the shape and volume of the electron cloud around a F⁻ ion. Anion-anion proximity changes further impact anion charge distributions. The differences in F charge distributions in the two salts indicates that the free energy contributions of F⁻ in the two systems will also be different.
The Bader volume is a function of the ion’s solvating environment, so changes to an anion’s environment will result in changes to the activity of the anion. Thus, the $\text{F}_2/\text{F}^-$ reaction has a unique electrochemical potential for each distinct cation environment and the use of a shared reaction between different salts is not a consistent reference.

In summary, the more conservative and best option when tabulating standard potentials in molten salts is to treat each salt melt as a separate solvent with its own EMF series\textsuperscript{236}. As stated previously, if data from multiple melts are combined into a single series, this should be clearly indicated to the reader and highlighted as an approximation. The following section gives an example of an EMF series constructed for a LiCl-KCl salt.

### 10.8 Redox Potential Series Based on the Infinite Dilution Standard State

We now present an Ellingham-type diagram of standard potentials vs temperature based on experimental data, which incorporates the principles that have been discussed up to this point. The data have been taken from Fusselman et al. and were obtained by them with respect to a silver-silver chloride electrode with $x_{\text{AgCl}} = 0.00477$ for the lanthanides and $x_{\text{AgCl}} = 0.00484$ for americium\textsuperscript{247}. Since data obtained by Yang and Hudson for the silver/silver chloride electrode in LiCl-KCl give confidence that these concentrations are in the infinite dilution region\textsuperscript{248}, the standard potential vs Ag/AgCl may be obtained as described previously. The standard potentials obtained in this way are tabulated in Table 10-4 and presented along with the $R^2$ values of the corresponding linear fits.
Table 10-4. Regressed standard potentials for various lanthanides and americium vs Ag/AgCl in LiCl-KCl eutectic. Data used in linear regression taken from Fusselman et al\textsuperscript{247}.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (K)</th>
<th>Standard Potential (V)</th>
<th>Fit R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Americium</td>
<td>673</td>
<td>−1.998</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−1.971</td>
<td>0.939</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−1.980</td>
<td>0.999</td>
</tr>
<tr>
<td>Cerium</td>
<td>673</td>
<td>−2.238</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−2.228</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−2.219</td>
<td>0.998</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>673</td>
<td>−2.196</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−2.187</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−2.178</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>748</td>
<td>−2.169</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>−2.159</td>
<td>0.997</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>673</td>
<td>−2.289</td>
<td>0.953</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−2.280</td>
<td>0.952</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−2.270</td>
<td>0.961</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>673</td>
<td>−2.226</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−2.217</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−2.207</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>748</td>
<td>−2.196</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>−2.187</td>
<td>0.998</td>
</tr>
<tr>
<td>Yttrium</td>
<td>673</td>
<td>−2.263</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>−2.255</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>−2.246</td>
<td>0.988</td>
</tr>
</tbody>
</table>

Table 10-5. Parameters for linear regressions of standard potential vs temperature for data from Table 10-4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intercept</th>
<th>Slope</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praseodymium</td>
<td>−2.491</td>
<td>0.0003935</td>
<td>0.999</td>
</tr>
<tr>
<td>Americium</td>
<td>−2.233</td>
<td>0.0003583</td>
<td>0.4334</td>
</tr>
<tr>
<td>Cerium</td>
<td>−2.497</td>
<td>0.0003854</td>
<td>0.9999</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>−2.558</td>
<td>0.0003989</td>
<td>0.9981</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>−2.443</td>
<td>0.0003665</td>
<td>0.9999</td>
</tr>
<tr>
<td>Yttrium</td>
<td>−2.501</td>
<td>0.0003535</td>
<td>0.9996</td>
</tr>
</tbody>
</table>
The potentials in Table 10-4 were then fit to a linear regression vs temperature, the results of which are shown in Table 10-5 and graphed in Figure 10-9. While americium had a poor $R^2$, the fit for the lanthanides is excellent.

![Figure 10-9. Emf series vs temperature for LiCl-KCl using the infinite dilution standard state. Temperature between 650 K and 800 K. Reference: Ag(I)/Ag (0) in LiCl-KCl at infinite dilution.](image)

This kind of diagram or table enables accuracy when predicting the potential of a particular component with known concentration. One merely needs to take the standard potential from Figure 10-9, or calculate it using the coefficients in Table 10-5, and use that together with the known concentrations for both the component under study and the reference electrode in Equation 10-17. As we have shown, with an infinite dilution standard potential, if the concentration of the known component is low enough, usually below 1 mol%, the activity coefficient term of Equation 10-12 can be neglected. This stands in contrast to diagrams such as
Figure 1 of the work by Zhang et al.\textsuperscript{179} which rely on pure-component thermodynamic data instead of experimental data. Figure 10-9 of this work may be used in conjunction with Equation 10-17 without an activity correction to accurately predict the potential of real cells; Figure 1 of the work by Zhang et al.\textsuperscript{179} cannot be used for this purpose as explained above.

10.9 Multiple-Anion Effects

Up to this point, we have considered minor components as salts whose anion is the same as that of the main salt mixture. We now use simulations to evaluate the impact of an unlike anion on the behavior of minor components. Specifically, AIMD simulations of CsI in molten LiF-BeF\textsubscript{2} eutectic (FLiBe) were performed and compared to similar simulations that utilized CsF instead of CsI. The interaction of cesium with surrounding F\textsuperscript{-} ions was characterized by the Cs-F pairwise radial distributions determined from the simulations.

These AIMD simulations were performed with the same software and basis sets as described in conjunction with the Bader Volume calculations presented earlier. Each simulation consisted of 98 FLiBe atoms and a varying number of CsF or CsI atom pairs randomly arranged via the PackMol software package, and was simulated under the NPT ensemble at 1 atm and 773 K. Each cell was run to equilibration before running for an additional 10 ps of simulation time for analysis.
Figure 10-10. RDF (fluoride density as a function of distance from the center of the cesium ion). (a) Raw RDF data. (b) Integral of RDF data.

Table 10-6. Cesium coordination with fluoride ions at various concentrations of CsF and CsI as calculated by AIMD simulations.

<table>
<thead>
<tr>
<th>Minor Component</th>
<th>Cs Concentration (mol%)</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF</td>
<td>4.55</td>
<td>13.94</td>
</tr>
<tr>
<td>CsF</td>
<td>6.67</td>
<td>14.36</td>
</tr>
<tr>
<td>CsI</td>
<td>4.55</td>
<td>10.82</td>
</tr>
<tr>
<td>CsI</td>
<td>10.64</td>
<td>9.18</td>
</tr>
<tr>
<td>CsI</td>
<td>17.65</td>
<td>7.52</td>
</tr>
</tbody>
</table>

The impact of the different anion (I\(^-\)) on the solution structure around Cs\(^+\) is shown in the radial distribution functions (RDFs) calculated using the VMD software package\(^{210}\) as shown in Figure 10-10. The abscissa of the first peak of each RDF represents the most probable distance between a Cs\(^+\) ion and a solvating F\(^-\). As shown in Figure 10-10a, the RDFs for Cs-F first peaks have nearly identical abscissa and termina. This indicates that the nature of the interaction between Cs and F changes very little due to the presence of iodide. However, the heights of the
peaks vary considerably. The implication of the differences in peak heights is evident in the number-density integral of the RDFs shown in Figure 10-10b. This integration yields the count of fluoride ions within a given radius of a central cesium ion. The integration over the entire first peak (that is, to the first minimum after the first peak) yields the coordination number.92, 98

Figure 10-10b shows that the number of F⁻ ions around Cs⁺ decreases in the presence of I⁻, and Table 10-6 shows the Cs-F coordination numbers. Comparison of the Cs-F coordination numbers for Cs cases with similar compositions (4.55 mol%) shows that the CsI minor component case has 22% less fluorides solvating each cesium than the CsF minor component case. Thus, the introduction of iodide reduces the quantity of Cs-F interactions. This is partly due to a reduction in the ratio of F to Cs when CsF is replaced by CsI in the simulation. However, the total number of fluoride ions in the simulation cell decreases by only two from the CsF case (58 F⁻ ions) to the CsI case (56 F⁻ ions), and the Cs-F coordination number decreases by roughly three fluoride ions per cesium in a box containing only two I⁻ ions. Simply substituting I⁻ ions for a small number of F⁻ ions in the salt structure at random does not account for the solvation changes of Cs⁺ observed in the two environments. Instead, the iodides are directly interacting with the cesium ions in place of fluorides. The larger ion size of iodide is evident in the reduction of Cs-F coordination by three fluorides per cesium (see Table 10-6) when only one iodide per cesium is present. In short, cesium prefers iodide in this environment, and fluoride solvation of cesium is interrupted by the presence of iodide.

In contrast to the addition of CsI, the addition of cesium fluoride to the fluoride melt did not appear to have a significant impact on the solvation and coordination of the minor component cesium. Specifically, a 32% decrease in the F:Cs ratio (from the 4.55 mol% CsF to the 6.67 mol% CsF case) had no substantial effect on the solvation of Cs⁺ by F⁻. Solvation is a
description of how a solvent “mixes” with a solute on an atomic level. If anion coordination
around a solute drastically changes, a change in activity of the solute will also be observed. Thus,
for cases where the anion of the minor component is identical to that of the base salt, any overall
changes to the cell potential of the salt mixture are consequences of changes to the minor
component cation concentration.

The introduction of a second type of anion species, iodide, does affect the solvation, and
by extension the activity, of individual cesium cations. Just as the activity of the fluoride anion is
a function of the composition of its solvating cations, the activity of the cesium in the FLiBe is a
function of the presence or absence of iodide. More generally, the activity of an ion is a function
of the composition of its solvating ions.

An infinite dilution standard state reference works well in molten salt systems because
short range cation-anion interactions dominate over short-range cation-cation or anion-anion
interactions. Thus, solutes of the same charge are much are less likely to be nearest neighbors
than solutes of opposite charge and the interactions of a dilute minor component cation are
primarily with the solvent for systems with a common anion.

Unlike anions in minor components present a couple of challenges. First, the nearest
neighbors of a cation are no longer constrained to be solvent anions, and solute-solute
interactions become much more probable. The infinite dilution standard is convenient because of
the physical insight on solute-solute interactions it provides; however, a system with multiple
anions may have a minor component cation activity that diverts from 1 at much lower
concentrations. Additionally, rather than a negligible change to the major anion activity, a new
activity term is needed for the minor component anion in order to correctly account for solute-
solute interactions.
10.10 Published Conclusions

This published work has examined the utility of an infinite dilution standard state for minor components in molten salts and compared it with a pure component standard state. An infinite dilution standard state has the advantage that the activity coefficients of minor components approach unity at low concentrations and can frequently be ignored with little loss in accuracy. In contrast, use of a pure component standard state is strongly dependent on the activity coefficient for minor components. This is because the pure component standard state less accurately reflects the actual conditions in the molten salt mixture, while infinite dilution correctly captures the fact that solute-solvent interactions dominate over solute-solute interactions for dilute minor components.

As a result, use of infinite dilution as a reference state enables treatment of minor components that is easier both in theory and in practical calculations involving real cells containing a minor component, since it does not require an activity coefficient correction at dilute concentrations. Under such conditions, the activity is equal to the concentration, which greatly simplifies analysis of important systems like those that involve corrosion. Thus, cell potential can be determined from concentration, and diagrams can be used to compare potential for different species at the same concentration. Such a diagram has been presented in this work. This cannot be done accurately for situations where the potential is strongly dependent on an unknown activity coefficient, which is frequently the case when a pure component reference is used.

Experimental data reveal that certain reactions proceed at very different potentials in different salt melts, and the present work examines why, using theory, experiment, and molecular dynamics simulations. We find that the chemical potential of the anion varies between
melts and that, more generally, the different cations present in each melt have an effect on other ions present, meaning that attempts to put, for example, all chloride melts on a universal scale vs Cl₂/Cl⁻, are at best an approximation. The most theoretically sound way to proceed is to treat each salt melt as a separate solvent.

Additional complications arise if the minor component includes an anion that is different than that of the base salt. Solute-solute interactions become significant at lower concentrations, and the mathematical convenience of using the infinite dilution standard state is reduced as cation activity can be disproportionally affected by the minor component anion, as shown in our AIMD simulations. Future simulation, experimental and theoretical work will examine these systems in more detail, as well as systems that include mixtures of minor components.
11 CESIUM FLUORIDE RETENTION AND VOLATILITY IN MOLTEN FLiBe

As demonstrated in Sections 7, 8, and 10, AIMD simulation results are extremely well-suited to collaborative studies with experimental supplements. Additionally, we have shown that cesium interactions with molten fluoride salts are a strong function of their environment and that certain cation-anion interactions will dominate over others. Due to cesium’s import as a major fission product, additional study into cesium solvation was merited. In the work presented below, we collaboratively examine the solvation stability of cesium fluoride in molten FLiBe and compare AIMD simulation observations with experimental measurements and observations. We discuss implications of computational insights on experimental observations and vice versa. The work presented, by Williams et al., is in preparation for submission at the time of this writing. Because a key requirement of this work is demonstrating that experimental behavioral predictions can be made from qualitative observations of phenomena in AIMD (see Section 5 of this work), the experimental portions of the work are included.

11.1 Introduction to Cesium Fluoride Retention and Volatility in Molten FLiBe

Molten salts are purported to have greater inherent safety in nuclear applications via radionuclide retention than alternative nuclear reactor designs. Here we examine the retention and volatility of cesium, as cesium fluoride, in LiF(66.7%mol)-BeF₂(33.3 %mol), or FLiBe, at 500, 650, and 800°C. We examine the solvation stability using inductively coupled mass
spectroscopy (ICP-MS) of experimental samples and also using ab initio molecular dynamics simulations. We find that cesium fluoride volatilization is negligible at temperatures up to 650°C. At 800°C, we observe minute but non-trivial solvation instabilities and volatilization of CsF.

The MSR design sports greater inherent safety when compared with the light water reactor design. The successful retention of radioactive fission products at near-atmospheric pressures is a major inherent safety feature of molten salt reactor designs.

Cesium dissolution is of interest because of its potential to spread harmful radiation. Cesium, in the form of the Cs-137 isotope was found as a metal particulate in the air after Chernoby249l, and continues to be the highest source of radiation at the Chernobyl nuclear accident site250.

We explore the solvation behavior of cesium in molten FLiBE in order to know its potential for release from a molten salt reactor. There are a variety of different molten salts that are worthy of study as possible coolants in MSRs. FLiBe was studied in our research. FLiBe is a molten salt made of a 2:1 mixture of lithium fluoride and beryllium fluoride that can be used as a coolant in a molten salt reactor.

The purpose of this paper is to determine if FLiBe can be used as a barrier to inhibit or slow cesium fluoride volatilization in a pebble bed reactor.

11.2 Methodology for Examining CsF Retention and Volatility in Molten FLiBe

The data were collected experimentally and computationally for temperatures of 500°C, 650°C, and 800°C. This temperature range generally represents MSR and FHR designs’ operating temperatures reported to the IAEA251. Both methods include a set of replicates at each temperature investigated. The Cs concentration of the experimental samples were measured
using inductively coupled plasma mass spectrometry. Ab initio molecular dynamics (AIMD) simulations were used to generate the computational data. These methods are detailed below.

Given that this discussion spans both atomic and macroscopic considerations, we note that some ambiguity exists when specifying mol fractions and molecular species in molten salts. For the purposes of this work, the molecular weight of FLiBe is defined as 32.96 g/mol, which is the molar-weighted average of the molecular weights of the binary salt components LiF (25.94 g/mol) and BeF₂ (47.01 g/mol).

11.2.1 Experimental Concentration Measurement

Cesium concentration was measured in CsF-FLiBe samples that had been melted and maintained at the specified temperature for varying time intervals.

Prior to performing any experiments, significant time was invested in developing adequate facilities and safety programs for handling beryllium materials. All experiments were performed in an anhydrous and anaerobic glovebox. Oxygen levels were consistently kept at 1-2ppm.

Beryllium exposure can lead to serious health effects. Sensitization is an immune response that can lead to Chronic Beryllium Disease. Unfortunately, the OSHA and DOE action limits are not based on any biological principle; therefore, it is crucial to minimize exposure as much as possible. BeF₂ poses extra challenges as it is water soluble and capable of migrating through skin. Animal studies have shown that sensitization can occur through dermal exposure. Most work was conducted inside the glovebox, where the beryllium hazard was contained; however, any inlet and outlet gas ports on the glovebox were fitted with HEPA filters to minimize particulate release. If FLiBe needed to be handled outside of the glovebox, then
operators donned coverall suits with full-face respirators. Once any beryllium material was returned to the glovebox, then the lab was cleaned so that swipe tests resulted in beryllium surface concentrations below the DOE free release limit of 0.2µg/100cm².

The FLiBe salt used for these experiments was provided by Kairos Power LLC and is denoted Flibe. The raw components of LiF and BeF₂ were mixed at a molar ratio of 2:1. The melted mixture was subjected to a proprietary purification based off the HF/H₂ sparging method developed at ORNL during the original molten salt reactor experiment. Once received, an additional purification step was performed. Batches of approximately 200g of Kairos Flibe were melted in 300mL nickel crucibles at 500°C. Once molten, a cube of pure beryllium metal was submerged into the salt for one hour then removed. The furnace was turned off and the salt was left to slowly cool overnight. This final purification step reduces any dissolved metal impurities while beryllium is oxidized. The reduced impurities gathered as a black sludge on the bottom of the crucible and as a thin metallic film on the top layer. These layers were removed so that salt without particulates was used.

Each test sample was prepared by mixing 1.065g Flibe with 0.100g CsF (99.99% Trace Metals Grade, Aldrich) to achieve a mixture of 2mol% CsF-Flibe. The granules for each component were mixed in a 15mL nickel crucible. The crucibles were prepared before use and cleaned between uses by submerging them in dilute HCl, rinsing with 18Mohm water, promptly vacuum drying, followed by immediate transfer to the glovebox.

CsF-Flibe samples were placed inside the furnace before any heating occurred. The furnace was set to the desired temperature (500°C, 650°C, or 800°C) with a full power ramp rate. Crucibles were removed when the furnace reached the desired temperature, then at 2, 4, and 8 hours after that point. At 800°C, several samples were analyzed after 24 hours at temperature.
The removed crucibles were carefully placed on the glovebox floor and allowed to cool. The salt melt within each crucible froze into a singular solid mass that could be digested for ICP-MS analysis. The salt masses did not adhere to the crucible surface once frozen; therefore, no residue or particulates that could detract from the final cesium concentration measurement were left over.

In total, 3 independent samples were prepared and tested for each time point at each temperature. The only exception being the 800°C 24h trials, where 6 samples were tested.

The solid sample masses were digested for ICP-MS analysis in 60mL PTFE vessels. The vessels were preloaded with 20mL 18Mohm water, 8mL HNO3 (67-70% Omni Trace, Millipore Sigma), and 4mL HCl (34-37% Omni Trace, Millipore Sigma). After dropping the mass into the digest solution and sealing the container, the vessels were placed into an oil bath at 115°C for over 24 hours until the mass was completely dissolved.

The digest solution was diluted with 2% HNO3 to a volume of 100mL. Subsequent serial dilutions were performed down to 1:20,000, as discussed below.

Analysis was performed using an Agilent 7800 ICP-MS with an inert sample introduction kit, PFA MicroFlow nebulizer, and sapphire 1.5mm sample injector.

800°C is the only temperature we examine above the melting point of pure CsF, which is 703°C\textsuperscript{252}. Experiments at 800°C are most likely to exhibit the highest CsF volatility. We thus consider results after 24 hours of thermal equilibration for data sets at that temperature.

The experiment used CsF salt, Beryllium, FLiBe, a nickel crucible, nitric acid, water, HCl, and digestion vessels. 0.1000g CsF was weighed out and placed in the nickel crucible, then 1.065g FLiBe was weighed out and placed in the same crucible with the CsF. This was repeated
for time periods of 2 hours, 4 hours, 8 hours, and 24 hours. Then the contents were mixed together to ensure the CsF would be able to dissolve with the FLiBe. Then the crucibles were placed in the furnace and heated to their respective temperatures of 500°C, 650°C, and 800°C at the highest ramp rate setting. The first crucible was removed when the furnace reaches the setpoint temperature to provide data for t = 0. Then each additional crucible was successively removed at 2, 4, 8, and 24 hours. Upon removal the salt melt cools and coagulates into one coherent mass.

Next, each Teflon vessel was filled with 20mL 18Mohm water, 8mL nitric acid, and 4mL hydrochloric acid. Each solidified salt mass was transferred from the nickel crucible to the Teflon vessel and the cap was screwed on. Then each Teflon vessel was placed in an oil bath at 115°C. It was left undisturbed for 24+ hours for digestion to properly occur. Afterwards, the digestion solution was transferred into a 100mL volumetric flask and diluted with 2% HNO3. It was diluted to 1:20,000 from the original 100mL digestion solution above. Then 10mL of 20,000x sample solution was placed in 3 polypropylene conical 15mL sample vials.

Then, the standards and samples were placed in the autosampler tray, and the instrument plasma was ignited and run through with 2% nitric acid for 10 minutes. Each set of samples at each temperature was run 3 separate times on the ICP-MS. This solution was analyzed 3 separate times.

The predicted average of cesium mass loss rate and the 95% confidence interval on the true cesium mass loss rate are reported. It should be noted that the measurements taken when the furnace-and-crucible system first reached thermal equilibrium (t = 0 hr) were not included in the regression of the data. The zero-hour data are still provided in the results section and are found to
agree with the predictions made by the regressed model. We discuss the reasons for excluding this time-set from our statistics in the 500°C portions of our results (see Section 11.3).

11.2.2 AIMD Simulation Details

Due to the discrete nature of an AIMD simulation, the concentrations of all species are fixed by the computational inputs. Additionally, the small atomic populations and timescales of AIMD make the direct simulation of the volatilization of a solute less feasible. However, the qualitative comparison of the solvation strength of a given solute-solvent combination across a range of temperatures is both feasible and well-suited to AIMD simulation.

Initial configurations of the atoms were generated using the Packmol software package\textsuperscript{124}. The temperatures studied were 500°C, 650°C, and 800°C. Each cell contained 120 atoms: 4 Cs atoms, 16 Be atoms, 32 Li atoms, and 68 F atoms. It should be noted that the CsF concentration in the experimental portion was 2.00mol% (8.58wt%) and in the AIMD simulations CsF concentration was 7.69mol% (27.74wt%). This much higher concentration is a function of the limited number of atoms in the AIMD simulations coupled with our desire to allow for solute-solute (Cs-Cs) interactions. Using 4 Cs atoms allows for the formation of non-linear Cs complexes in addition to simpler Cs complexes. Seeing that a CsF composition of 7.69mol% correlates to a simulation containing only 4 cesium atoms, it is clear that significantly lower compositions are not feasible without much larger simulations. Many Bothans died to bring us this information\textsuperscript{117}. However, the rupture of a TRISO particle and subsequent release of Cs into the coolant salt would likely be followed by local CsF concentrations much higher than the expected bulk CsF concentration. Therefore, the AIMD simulations lend insight into high local concentrations.
To facilitate a timely equilibration, each simulation contained an arrangement of roughly proximal Cs ions in a planar ‘Y’ shape, as shown in Figure 11-1. This configuration allowed for Cs dissolution because of the relatively high surface area of the Cs complex, but also facilitated the possible formation of a tighter, lower surface area Cs complex.

The atoms were added to a cubic simulation cell in random order. The initial lengths of the cells at 500, 650 and 800°C were 11.4Å.

The AIMD simulations were performed using the CP2K software package. The AIMD simulations utilized density functional theory (DFT) to numerically approximate the solution to the Kohn-Sham equations at every molecular dynamics (MD) step. We employed the Perdew-
Burke-Ernzerhof exchange-correlational functional\textsuperscript{118}. The Generalized Plane Waves method (GPW)\textsuperscript{122, 161, 204} was utilized to approximate the electron density of the simulated systems.

We modelled the atoms using DZVP-MOLOPT-SR-GTH gaussian basis sets\textsuperscript{163} and used Goedecker-Teter-Hutter (GTH) gaussian type pseudopotentials\textsuperscript{90, 164} to treat the core electrons. The temperature was moderated with the canonical sampling through velocity rescaling (CSVR) thermostat\textsuperscript{253}. Bussi et al. concluded that this thermostat was more ergodic than the Nosé-Hoover algorithm\textsuperscript{166, 253}. This process has been found to accurately predict behavior of other molten fluoride salts and solutes\textsuperscript{1, 2, 4, 50, 74, 92, 119}.

Three simulations of molten FLiBe with CsF were conducted at each temperature of interest for a total of nine simulations. A molecular dynamics (MD) timestep of 0.5 fs was employed and the NpT ensemble was used in conjunction with the periodic boundary condition. The system pressure was held at 1 atm by a CSVR barostat\textsuperscript{166, 253}. The density of a molten salt is incredibly sensitive to minute changes in the system’s energy\textsuperscript{2, 98} and so we used density stability over time as our metric of equilibration\textsuperscript{1, 2, 4}. The simulations each include a 50 ps equilibration period and a subsequent production period of at least 20 ps. Only data from the production portion of the simulations is considered in our analysis.

AIMD simulations are well suited to analyzing the structure of molten salt systems\textsuperscript{2, 50, 54, 55, 73, 75, 92, 98, 99, 101, 254}. The trajectories of the ions generated during the AIMD simulations can be used to compute the pairwise radial distribution functions (RDFs) of the ions.

RDFs yield important structural and behavioral information about atomic systems, and have been employed to explore Cs interactions with molten FLiBe previously\textsuperscript{4}. In this work, we examine the structure of Cs in each of the temperatures of interest by comparing the Cs-Cs RDFs. The number-density weighted integrals of the Cs-Cs RDFs are also examined. Our RDFs,
normalized integrals, and atomistic visualizations are generated using the VMD software package\textsuperscript{210}.

The Cs-Cs RDFs were averaged with other RDFs at the same temperature. The normalized integrals of these RDFs were also averaged with other normalized integrals of RDFs at the same temperature. This greatly improves the clarity of comparing the Cs structures at the three temperatures in question.

A second analysis technique was used in which the average distance between all Cs ions was calculated at each time step. Because of the statistically low number of Cs atoms in the simulation, a simple moving average of the previous 0.4 ps of data was applied to remove some noise and make the data more readable.

11.3 CsF Retention Study Results and Discussion

Both approaches of our research yield convergent results. We find that CsF is noticeably volatile at 800˚C but is relatively nonvolatile in the 500-650˚C range. We will first examine the experimental results and second the results from the ab initio molecular dynamics simulations.

11.3.1 Experimental Results

In the experiments at 800˚C, we find that the ratio of the final and initial masses of Cesium decreases steadily over time, as shown in Figure 11-2. While the predicted average mass-loss rate of Cs is 0.72%/hr, the 95% confidence interval (C.I.) on the true average mass-loss rate is relatively large and includes a zero mass-loss rate. We extend our 95% C.I. regression to include the additional data taken after 24 hours of thermal equilibrium at 800˚C, as shown in Figure 11-3.
Figure 11-2. Cesium mass loss ratio over time in FLiBe at 800˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown.

Figure 11-3. Cesium mass loss ratio over time up to 24 hours in FLiBe at 800˚C. The 95% Confidence Interval bands for the mean and single point predictions are also shown.
Here the Cs loss is more pronounced. The predicted average mass-loss rate of Cs increases to 0.83%/hr when including data from the 24-hour set. Further, the 95% C.I. on the true average mass-loss rate of Cs no longer includes a zero mass-loss rate. The C.I. mean prediction bounds suggest that the true average mass-loss rate of Cs is at least 0.61%/hr with 95% confidence.

While the actual loss of Cs from a molten salt solvent with a given surface area is most likely an exponential decay function as the molar concentration of Cs decreases, a linear function seems adequate over the relatively small concentration changes we observe.

No solid particulates or liquids are removed from the crucible during the experiment, thus we conclude that the loss of Cs is through volatilization. This will be examined more fully in after reviewing the AIMD portion of our results.

![Figure 11-4](image.png)

Figure 11-4. Cesium mass loss ratio over time in FLiBe at 650°C. The 95% Confidence Interval bands for the mean and single point predictions are also shown.
In the experiments at 650°C, the predicted average mass-loss rate of Cs is only 0.16%/hr, as shown in Figure 11-4. The Cs mass-loss rate at 650°C is only 19.3% of the Cs mass-loss rate at 800°C. Additionally, the 95% C.I. bands on the experimental results at 650°C include a wide range of possible mean predictions, making the exact mass-loss rate somewhat uncertain. We can say that the Cs loss is not extreme, so while some Cs loss at this temperature is likely, the average rate of volatilization seems greatly decreased from the 800°C cases. Considering the relatively high melting point of pure CsF (~704°C)\textsuperscript{252}, this is not overly shocking.

In the experiments at 500°C the average mass-loss rate of Cs is very similar to the 650°C cases.

Figure 11-5. Cesium mass loss ratio over time in FLiBe at 500°C. The 95% Confidence Interval bands for the mean and single point predictions are also shown. The data shown at t = 0 was not included in the regression.
It should be noted that the measurements taken when the furnace-and-crucible system first reached thermal equilibrium where not included in the regression of the data at 500°C. As can be seen Figure 11-5, the Cs mass ratios from measurements at 0 hours are considerably lower than 1. This is not overly problematic in itself, but when compared with measurements taken at 2 and 4 hours, it appears that the mass of Cs increases over time.

We note that for the combination of this temperature (500°C) and this duration (0 hours) only, a phenomenon was observed during the acid digestion phase of preparing the samples for ICP-MS. When the digestion acid was first poured onto the surface of the solid salt sample, an unknown vapour product was consistently observed to form on certain regions of the surface which visually appeared unremarkable. This phenomenon was not observed for samples of longer durations at this temperature or at any other temperature. We speculate that the composition of this vapour product includes Cs. This is indicative of a relatively slow rate of dissolution of CsF at 500°C, which we will discuss further after considering additional insights from our AIMD results.

### 11.3.2 AIMD Results

Our AIMD simulation results confirm and inform our experimental findings. The Cs-Cs Radial Distribution Functions (RDFs) for each temperature are given in Figure 11-6. The relative noise in the RDFs is a function of the limited quantity of Cs ions in each simulation. A reference line is added at g(r)=1 for convenience. The neighbor functions for these RDFs are shown in Figure 11-7. A reference line is also added, which approximates the neighbor function of Cs-Cs in the theoretical case where Cs structuring is truly random.
Figure 11-6. Radial Distribution Functions (RDFs) for Cs-Cs pairs in FLiBe at 500˚C, 650˚C, and 800˚C. A line has been added at \( g(r) = 1 \) over the range 3.7-8.0 Å for reference.

Figure 11-7. Neighbor Functions for Cs-Cs pairs in FLiBe at 500˚C, 650˚C, and 800˚C. A line has been added for the normalized integral of \( g(r) = 1 \) over the range 3.7-8.0 Å for reference.
From the AIMD simulations of CsF in FLiBe at 800°C, we see that the Cs ions are not well solvated by the bulk FLiBe. The Cs ions form a planar complex as shown in Figure 11-8. This complex is localized to a single, small region of the total cell volume. This reduces the total interface area between Cs ions and the bulk of the molten salt solution relative to 4 spatially separated (or well-mixed) Cs ions.

Figure 11-8. Visualization of an equilibrated AIMD simulation of CsF in FLiBe at 800°C. Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow.

Over the course of the simulation, the Cs-Cs interactions are never interrupted by other cations. This behavior indicates that the Cs solute is not well solvated within the salt\textsuperscript{215} and is apt to leave solution should it encounter a nucleation site or phase boundary. This behavior has been
observed in AIMD simulations of other molten salt systems with solutes that are known to leave solution\textsuperscript{2,215}. This behavior does \textit{not} indicate which phase the solute is more likely to form \textit{en masse}, only that it is not energetically favorable to solvate the solute ions individually.

While all three simulations at 800°C had complete Cs complexation, none of the three simulations at 650°C had any additional Cs complexation beyond the original configuration (see Figure 11-1), and the equilibrated simulations show Cs ions that are spaced much farther apart, creating a maximum area of solvation interface with the FLiBe salt, as shown in Figure 11-10. This complete solvation of Cs ions by the FLiBe salt is shown quantitatively in Figure 11-6 and Figure 11-7. The RDF for Cs-Cs pairs at 650°C shows a clear second peak which is significantly taller (~160\%) than the first peak. Additionally, the neighbor function for the 650°C simulations is consistently below the reference line, that the Cs ions have a less than random chance of being located within up to 7 Å of one another. This indicates that Cs ion interactions with the salt are much more favorable at 650°C than at 800°C.

The favorable dissolution of Cs complexes in the 650°C simulation was confirmed by the analysis measuring average Cs-Cs distance over time as shown in Figure 11-9. It is worthwhile to note that the Cs cations in the simulation that ran at 650°C are significantly further apart than half of the box length. This indicates that their dispersion is more pronounced than a simply random distribution.
That solute-solvent interactions should dominate so completely over solute-solute (Cs-Cs) interactions suggests that Cs has no strong motivation for leaving the salt at this temperature.
We observe complete Cs complexation in all our simulations at 500°C. However, the form of the Cs complex is less structured than the planar complexes observed at 800°C. At 500°C, the Cs complexes form a loosely disphenoidal structure as shown in Figure 11-11. The Cs complex is somewhat amorphous, with Cs-Cs distances varying considerably, as evidenced by the width of the RDF first-peak in Figure 11-6. However, the first-peak height and abscissa agree
well with the RDF for the simulations at 800°C. This suggests that Cs is not well-solvated in FLiBe at 500°C.

Figure 11-11. Visualization of an equilibrated AIMD simulation of CsF in FLiBe at 500°C. Cs ions are blue, F ions are green, Li ions are purple, and Be ions are yellow.

11.3.3 Additional Discussion

With the combined insight of the experimental and computational results, we can more soundly arrive at joint conclusions. First we consider the 800°C case. At this temperature, Cs is seen experimentally to steadily disappear from the salt and is seen computationally to solvate
poorly with the salt. We conclude that at 800˚C Cs volatilizes from molten FLiBe in the form of CsF.

The overall flux of the Cs volatilizing from the molten FLiBe can be found by estimating the surface area of the sample and then dividing the rate of mass loss by the surface area. Dividing the rate of mass loss by the area yields an overall flux of 0.0023 g Cs/(cm²/hr). In the event where there is a major reactor accident where the molten salt is exposed to the ambient environment, the release impact of the Cs and its isotopes can be calculated using this flux. For example, the “Mark 1” Pebble-Bed Fluoride-Salt-Cooled High-Temperature-Reactor (PB-FHR) has a diameter of 3.5 meter. In the event of an accident where the top of the PB-FHR was exposed, the reactor would suffer a loss of approximately 62.4g/hr Cs-137 to the ambient environment.

For the 650˚C case, Cs is not seen experimentally to significantly volatilize and is seen computationally to prefer complete solvation by the bulk FLiBe salt. We conclude that, at this temperature, CsF has a relatively high solubility limit ( > 7.69mol%) in FLiBe and is not a serious volatilization risk.

For the 500˚C case, Cs is not seen experimentally to significantly volatilize but is seen computationally to prefer complexation over solvation in the bulk FLiBe salt. The complexation observed in the AIMD simulations seems to suggest that CsF may rapidly precipitate out of solution at 500˚C and 7.69mol% CsF, however the wide peaks in the Cs-Cs RDF more likely indicate that CsF simply has a slower rate of dissolution.

Additionally, experimentally we note the loss of CsF during ICP-MS sample preparation for the samples removed from the furnace upon reaching the setpoint. The formation of Cs-bearing vapour is known to be a product of the acidic dissolution of CsF. The increase in the Cs
mass ratios in samples from subsequent times, coupled with the bubbling reaction observed during ICP-MS sample preparation indicates that for the zero-hour samples, the CsF was found more abundantly on the sample surface where a gas-phase product would be less likely to become entrained in ICP-MS digestion acid, and retained in the sample.

We speculate that incomplete dissolution of CsF in the molten FLiBe for the zero-hour samples resulted in larger Cs complexes and particles being pushed to the salt surface during freezing. This would explain the unusually high CsF surface concentrations necessary to form and release significant Cs-bearing vapour product during ICP-MS sample digestion. However, samples with longer furnace durations achieved better dissolution, resulting in smaller, better solvated Cs structures. These simpler structures are more easily integrated into a crystal lattice structure typified in solid salt and therefore significantly less Cs was pushed to the surface during freezing. The sample with larger, less-dissolved Cs structures near the surface are much more likely to fail to entrain any Cs-bearing vapour products of the digestion reaction. Thus, the Cs mass ratios for the samples with longer furnace durations more closely match unity, as considerably less Cs was lost during sample digestion.

It is noteworthy that this conclusion is informed by both experimental and computational observation. We suggest that such a dual approach has many potential applications for understanding molten salt chemistry.

Fitzhugh et al. have shown that the solvation shell of Cs in molten FLiBe is a function of other minor solutes, and that the presence of iodide in the salt impacts the solvation behavior of Cs even at small ratios of I:Cs$^4$. Because the solubility of Cs in FLiBe is a measure of how well it solvates within FLiBe, it follows that the presence of other minor component ions such as iodide will affect the solubility of Cs in FLiBe$^4$. A theoretical rupture of a TRISO fuel pebble would
result in the simultaneous introduction of multiple fission products into the molten salt. Any Cs in the TRISO would be quite proximal to other minor components, including iodide, at the moment of dissolution. Additional work should be done in investigating these solute-solute impacts on Cs release from FLiBe.

11.4 Conclusions on CsF Retention and Volatility in Molten FLiBe

Both approaches of our research yield convergent results. We find that CsF is noticeably volatile at 800˚C but is relatively non-volatile in the 500-650˚C range.

We find that the rate of dissolution of CsF in FLiBe is not trivial at temperatures below 800˚C, but that the solubility limit of CsF in FLiBe at 500˚C is > 2mol% and at 650˚C is > 7.69mol%.

The potential for bilateral investigation of molten salts using experimental and computational means is demonstrated to be effective. Further such studies aimed at the impacts of iodide on cesium retention would be in order.

By finding the mass-loss rate and flux of Cs in FLiBe, these results can be used to help estimate the amount of Cs lost during reactor operations or during reactor accidents. These would be especially useful for Cs isotopes like Cs-137 when estimating the impact of reactor accidents.

We have successfully demonstrated that qualitative observation of AIMD simulations of molten salt systems can inform conclusions based on experimental observations, satisfying one of our requirements (See Section 5).
12 WATER, NICKEL, AND NICKEL OXIDE BEHAVIOR IN MOLTEN FLINaK

12.1 Introduction to Water, Nickel, and Nickel Oxide Behavior in Molten FLINaK

Several ab initio simulations were performed to investigate how water interacts with the molten salt FLINaK with and without the presence of Ni. The removal and continued of water from the salt is a key design objective of molten salt research because of the impact of water on corrosion and fuel oxidation. Uranium oxides in particular are known to be insoluble in molten salts.

Several questions were posed by experimental collaborators which we explore. First, if water exists in the salt, does it appreciably disassociate? Second, if HF forms, does it leave the salt? This phenomenon would have an impact on sparging of HF and salt purification\textsuperscript{255}. And third, does water react with certain solutes, in particular Ni? Ni has previously been used in characterizing an appropriate reference electrode for FLiBe\textsuperscript{256}. We designed simulations to explore these questions. This study was designed as a collaborative work and possible publication.

12.2 Study on Water, Nickel, and Nickel Oxide Behavior in Molten FLINaK

Initial simulation configurations were prepared using PACKMOL and performed using CP2K. The simulations used the CP2K, DFT, and MD settings outlined in Sections 0, 7, 8.2, and
9.2. The simulations were given 20 ps to equilibrate. Only data collected after this equilibration period and the simulation had achieved a stable density were analyzed.

Four systems were investigated at 873 K. Pure FLiNaK, FLiNaK with one water molecule, FLiNaK with one nickel atom, two additional fluoride atoms and one molecule of water, and FLiNaK with three nickel atoms, three oxide atoms, ten hydrogen atoms, and ten fluoride atoms. Each system contained 100 FLiNaK atoms as a base, to which any solutes were added, including additional fluoride ions.

To study these systems several approaches were taken. The average distance between atoms of the same element vs time was used to analyze specific homoelemental interactions and also to examine the overall structural stability of the system. In this work this is referred to as the mean distance to homoelemental neighbours (MDH). This MDH technique was also used to confirm the sodium ordering observed in the FMgNaK structure study (See Section 8.4). The second approach was the traditional radial distribution function (RDF). A third, a dynamic RDF (DRDF), where the RDFs are calculated for each picosecond segment and the array of RDFs are combined into a 3-D ($\rho$, t, $g(r)$) surface, was used in the analysis but is not shown here. The DRDF provides an additional dimension to the standard RDF, while still maintaining strong statistical strength. Each individual RDF in our DRDF analyses has 200 samples per interaction. For more information on the DRDF, please contact Clark et al. Finally, Bader volumes were used to explore the interactions between ions of disparate nature, such as the F-H-F structure.

Only one simulation of the pure FLiNaK system was conducted. This was included as a benchmark for the other systems, and is also in good agreement with other pure FLiNaK simulations this research group has conducted. The MDH for this simulation is shown in Figure
12-1. The relative noise of the Na function is at least partially caused by the smaller Na population in the salt. The Na ordering observed in Section 8.4 may also occur in FLiNaK, but this conclusion is outside the scope of this work.

Figure 12-1. The mean distance to homoelemental neighbours (MDH) for FLiNaK constituents in a simulation at 873K.

For the comparisons of water disassociation with 100 FLiNaK atoms, 2 H atoms, and an O atom, three simulations were used. In the first, we added the solutes as a water molecule, the second as an H\(^+\) and OH\(^-\), and the third as totally disassociated H\(^+\), H\(^+\), and O\(^-\) ions. For ease of comparison, the simulations were run in NVT instead of NpT. The cells were constrained at a cubic length of 12.07348 Å. This number was based on the equilibrium volume of previous
FLiNaK and water simulations cells which are not published, but which were created at the same time as the published simulations reported in Sections 7 and 9.

No disassociation or association reactions were observed, however the system energies for the three simulations are shown in Figure 12-2. The potential energy of simulations of FLiNaK at 873K containing 2 H atoms and 1 O atom. Figure 12-2. From this observation, it seems likely that the most stable form of the constituents of a water molecule in molten FLiNaK are a water molecule. It is noted that an examination of the transition states was not conducted, and the relative activation energies of partial and complete disassociation and association are unknown. The MDH for the simulation including the intact water molecule is given in Figure 12-3.

Figure 12-2. The potential energy of simulations of FLiNaK at 873K containing 2 H atoms and 1 O atom.
An additional three other systems were simulated to investigate water’s oxidation of nickel in FLiNaK at 873 K. A nickel atom was artificially placed 1.75 and 4.0, and 10.45 Angstroms away from the oxygen of the water molecule to test if Ni oxidation was a strong function of diffusion. 2 F atoms were also added at large distances from the water molecule (~7.5 Angstroms) to balance the total simulation charge. In the 1.75 Angstrom cell, we note that the Ni-O positioning was coordinated with the water molecule’s hydrogens oriented away from the Ni atom, such that the Ni-H$_2$O complex formed a trigonal planar structure as shown in Figure

Figure 12-3. The mean distance to homoelemental neighbours (MDH) for FLiNaK with H2O elemental constituents in a simulation at 873K.
Yet, in all three simulations, no Ni oxidation was observed. In fact, the 1.75 Angstrom simulation showed strong repulsion between the Ni and O ions, resulting in nearly immediate separation of the two that was sustained by the salt solvent for the duration of the simulation. While Ni-H$_2$O reactions are still very plausible, we have obtained no direct evidence of their transpirations.

The fourth system contained 100 FLiNaK atoms, 10 H atoms, 10 additional F atoms, 3 Ni atoms and 3 O atoms. Only one simulation was conducted for this simulation, due to the heavy computational resources required for DFT calculations of Ni atoms. The basis-set and pseudopotential chosen for Ni includes 18 outer electrons in the basis set. Including 3 Ni atoms made this simulation quite sluggish, but also quite informative.
The MDHs for this system, including the equilibration portion, are given in Figure 12-8. We observe that the MDH functions for Ni and O dip at ~10 ps. This is caused by the formation of a Ni-O chain, which is shown in Figure 12-5. The solubility of NiO complexes is thus likely to be low. Interestingly, the excess HF also seems somewhat unstable in the melt, and in Figure 12-6 it is shown that fluorides in close proximity to H atoms can be found on the edges of the simulation, and not well mixed in the bulk salt. The HF is then not well solvated and apt to leave the salt. The Ni-O structure is shown adjacent to, but not solvated by the HF microphase. Thus, the sparging of HF likely causes salt purification for physical phase-boundary reasons, and it is possible that chemical interactions play a much smaller role in its efficacy.

Figure 12-5. Ni-O chain formation within molten FLiNaK at 873 K in the presence of excess HF.

On the stability of the F-H-F complex (which is the solvated form of HF$_2$ and was also observed in the simulations discussed in Section 9.3.2), we turn to the Bader volume
decomposition for insights. The Bader volumes for two fluoride ions which surround a hydrogen ion are shown in Figure 12-7.

Figure 12-6. Ni-O structure observed in FLiNaK at 873 K in the presence of excess HF. The HF structures are also accented, but the bulk salt cations and any F- ion great than 2 Angstroms from an H+ ion are faded.

Figure 12-7. Bader volumes for 2 F- ions are shown enveloping an F-H-F complex in molten FLiNaK at 873 K.

The size of the fluoride Bader volumes in Figure 12-7 and their clear overlap in the region surrounding the H+ ion suggest that the H+ ion is well-shielded electronically, and that the
oblong ionic complex is quite stable. The shape and size of the F-H-F complex is disruptive to the normal salt structure, and this makes integration into the bulk salt complicated, fortifying the notion that H-F is relatively volatile in molten fluoride solutions.

Figure 12-8. The mean distance to homoelemental neighbours (MDH) for FLiNaK with Ni, O, and H elemental constituents in a simulation at 873K.

12.3 Conclusions from the Study on Water, Nickel and Nickel Oxide Behavior in Molten FLiNaK

Based on the observations available from the simulation data there is no reason to believe that the standard sparging procedure would be ineffective in removing H₂O from FLiNaK. H₂O
is solvated well in the salt and should be removable by bubbling an inert gas through the system. H₂O never oxidized Ni in our simulations.

HF is not well-solvated by molten FLiNaK and should be expected to volatilize out of solution. If HF is solvated in or sparged through molten FLiNaK then a likely configuration is HF₂⁻. This complex seems unlikely to react with metal oxides because of the shielding of H. Quasi-stable complexes will likely be perturbed by the passing of the HF phase, facilitating salt purification.
13 ONGOING PROJECTS AND FUTURE WORK

The following is a list of projects, mostly collaborative in nature, which have been initiated but not concluded and are relevant to this dissertation. The duty of concluding these works rests predominantly on others besides the author, but contributions have been made and possible outcomes are worth noting.

In a follow-up study to that presented in Section 7, Frandsen et al. will explore the RDFs of FLiNaK with minor concentrations of Zr and Cs to determine the impact of minor components (~1 atom%) on RDFs. The simulation work for this study has been completed and the RDFs created, but their analysis sans the neutron diffraction results is not impactful. The neutron diffraction experiment and results are expected Fall 2021.

Additional pure salt simulations of FLiNaK, FLiNaTh, PuNaCl, ThNaCl, LiFTh, FLiNaU, and FLiBe have been initiated by the research group, and will include larger temperature ranges to examine liquid density and structure trends at higher temperatures, as well as diffusion coefficients at temperatures of interest. This work is expected to conclude late 2021.

Last but most prominent, force-fitting efforts of pure salts, including simple binary salts, are underway to enable MD simulation of larger, more statistically significant molten salt systems, and are expected to be presentable by Fall of 2021. In addition, the tools to calculate several the thermophysical properties mentioned in Section 4.1 have been developed.
Future work by the research group may include a follow-up study to the work presented in Section 11, which would examine the effects of other elements such as iodide and cerium on cesium volatility and retention in molten FLiBe and FLiNaK. Widom particle insertions will also be conducted to determine the solubility of solutes of interest, as demonstrated to be feasible in molten salt solutions by Liu et al\textsuperscript{257}.
14 CONCLUSIONS

The goals of this work as listed in the Introduction, are first, to know the basic thermophysical properties of molten salt mixtures. Second, to know what ionic complexes form. Third, to predict how adding another trace contaminant will alter these properties and complexes, at least at a basic level. This work has accomplished these goals.

In Sections 7 and 8, we have demonstrated AIMD’s capacity to produce density and self-diffusion property data. In Sections 9-12, we have identified molten salt complexes of interest and attached them to thermodynamic principles such as electrochemical potential and solubility. In Sections 9, 10, and 11 we have explored the impacts of minor components on each other and on the salt.

AIMD simulations facilitate the drawing of insights on molten salt structure and properties directly. AIMD simulation work greatly supplements and is supplemented by experimental work. The advantageous symbiosis of computational and experimental collaborations on molten salt research, both in problem definition and resolution, merits additional work. Work done AIMD simulations can easily be repurposed for force-fitting an interatomic potential model for classical molecular dynamics (MD) simulations, from which more statistically sound thermophysical properties can be computed.
General trends and insights about molten salt behavior have been accessed via AIMD simulation. While quantitative models for all of these trends are beyond the scope of this work, the collection of trends and insights will be valuable in the future development of such models.

Anions are much more voluminous than cations of comparable masses; for any given solute, its solvation shell is predominantly comprised of anions unless it is both strongly negative and of a comparable size to some cation components. Solutes that do not follow this corollary can be considered to be poorly solvated.

Anions are much more polarizable than cations of comparable masses; because the polarization and deformation of anions is much more typical than the deformation of cations, the salt structure of a single-anion salt can be modeled as a semi-rigid cation lattice through which anions fluidly squeeze as they diffuse. The energetic costs of polarization during diffusion are bourn almost exclusively by anions as the polarization costs for anions are so much lower. Viscosity trends among like-structured salts are thus likely to be a much stronger function of the anion than the cation.

The combination of these two ionic qualities results in an environment where minor component solute-solute interactions can be accurately modeled by Henry’s law at unexpectedly high concentrations\(^4\).

Accurate salt structure\(^1\), energy, and density are all needed to confirm AIMD equilibration. The requisite equilibration time for AIMD simulations of molten salts is longer than commonly expected, and cation structuring suggests that random initial configurations are not well-suited to AIMD simulations.
The coordination of solutes is a useful analysis of oxidation and stability\(^2\). Oxygen will readily attack metal ions. The formation of H\(_2\) with hydroxides in the presence of HF in molten fluorides is possible. HF is mildly soluble, but also reasonably volatile.

Accurate AIMD simulations of molten salts require ludicrously high plane-wave energy cutoffs to distribute the electron density field accurately in an ionic and non-covalent manner. Molten salt melts have electron fields with unusual disparity between local charge minima and maxima which is not well modelled by the non-preferential charge distribution of the generalized planewave density functional.

In addition to being both more polarizable and voluminous, anions of halide salts also account for a minimum of 50\% of the atomic composition. Halide salts with divalent or multivalent cations have even larger atomic fraction of anions. Thus the impacts of including VdW dispersion corrections\(^2\) are most keenly felt by the anions, and behavioral impact studies should begin by exploring anionic behavioral differences.

In conclusion, AIMD simulations of molten salts is an indispensable tool to exploring the chemistry of molten salts.
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