The Pennsylvania State University

The Graduate School

Intercollege Program of Materials Science and Engineering

DETERMINATION OF FUNDAMENTAL THERMODYNAMIC PROPERTIES OF ALKALI/ALKALINE-EARTH ELEMENTS IN LIQUID METALS FOR RECOVERY FROM MOLTEN SALT SOLUTIONS

A Dissertation in

Materials Science and Engineering

by

Nathan D. Smith

© 2018 Nathan D. Smith

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

December 2018

The dissertation of Nathan D. Smith was reviewed and approved * by the following:

Hojong Kim

Assistant Professor of Materials Science and Engineering

Dissertation Advisor

Chair of Committee

Allison M. Beese

Assistant Professor of Materials Science and Engineering

Zi-Kui Liu

Distinguished Professor of Materials Science and Engineering

Thomas Mallouk

Evan Pugh University Professor of Chemistry, Biochemistry and Molecular Biology, Physics, and Engineering Science and Mechanics

Suzanne E. Mohney

Professor of Materials Science and Engineering

Chair of the Intercollege Graduate Degree Program in Materials Science and Engineering

*Signatures are on file in the Graduate School.

Abstract

In the nuclear industry, uranium is recovered from used nuclear fuel using a process known as electrorefining in which a metallic used nuclear fuel anode is oxidized into molten LiCl-KCl-UCl₃ electrolyte and pure U is preferentially reduced onto an inert cathode. While electrorefiner systems facilitate the recycling of substantial amounts of uranium from used nuclear fuel, they also contribute to the production of nuclear waste due to the build-up of dangerous elements including ⁹⁰Sr and ¹³⁷Cs in the molten salt electrolyte as they are more active in the salt than U and will therefore oxidize out of the anode before U. The accumulation of Sr and Cs in the electrolyte presents a problem as Sr and Cs isotopes have high heat densities and produce large amounts of highly ionizing radiation; these hazards combined with difficulty in removing the highly stable Sr and Cs from the electrolyte necessitates frequent replacement and disposal of the electrolyte, which then contributes to the overall volume of nuclear waste. This dissertation focuses on evaluating the viability of using liquid metal electrodes as a method for electrochemical separation of Sr and Cs from LiCl-KCl-based molten salts due to their strong atomic interactions with alkali/alkalineearth elements, which cause a shift in relative stability of the alkali/alkaline-earths in the electrolyte.

Thermodynamic properties, including activities, partial molar entropies, and partial molar enthalpies, were determined using electromotive force measurements for the Sr-Bi, Sr-Sb, and Sr-Sn binary systems in order to elucidate the strength of interactions between Sr and each liquid metal. By combining the fundamental thermochemical data with phase characterization of each of the binary systems using X-ray diffraction (XRD) and differential scanning calorimetry (DSC), a comprehensive understanding of both thermodynamic phase behavior was developed for all three binary systems. Activities as low as $a_{Sr} = 10^{-13}$ at $x_{Sr} = 0.04$ at T = 888 K were measured as well as liquid state solubilities as high as 40 mol% at 988 K. Experimental data was used as input data towards computational efforts involving first-principles calculations as well as the CALPHAD technique in the case of the Sr-Sb system to develop an improved Sr-Sb phase diagram and provide further basis for the use of computational models in elucidating strongly interacting binary systems.

Attempts to remove Sr from molten salt electrolyte using an electrochemical cell with liquid metal (Bi, Sb, Sn) cathodes were successful, with post-mortem elemental analysis of the electrodes confirming significant quantities of Sr (4.0-6.5 mol%) deposited into Bi and Sb. Furthermore, deposition results correlated well with the deposition behavior predicted from the aforementioned electromotive force measurements, inviting the possibility of using liquid metal electrodes as a method for selectively removing Sr from molten LiCl-KCl electrolyte and for reducing the total volume of nuclear waste left accumulating in on-site repositories throughout the US.

Table of Contents

List of Figur	res	vii
List of Table	es	X
Acknowledg	gements	xii
Chapter 1.	Introduction	1
1.1 Ele	ectrochemical Separation	1
1.1.1	Nuclear Waste and Electrorefining	1
1.1.2	Challenges with alkali/alkaline-earth fission products in electrorefining	5
1.1.3	Alkali/Alkaline-Earth Interactions with Liquid Metals	6
1.1.4	Application to Purification of Electrorefiner Molten Salts	10
1.2 Dis	ssertation Overview	12
Chapter 2. Systems	Determination of Fundamental Thermodynamic Properties for Sr-M Binary 13	
2.1 Ele	ectromotive Force Method	13
2.1.1	Electrolyte Selection	14
2.1.2	Electrode Fabrication	18
2.1.3	Electrochemical Cell Assembly	19
2.1.4	Electromotive Force Measurements	21
2.1.5	Calibration of the $x_{Sr} = 0.10$ Reference Electrode	22
2.1.6	Calculation of Thermodynamic Properties (ΔSSr , ΔHSr , $\ln(a_{Sr})$, $GSrE$)	25
2.2 Str	ontium-Bismuth Binary System	29
2.2.1	Literature Review of Sr-Bi	29
2.2.2	Electromotive Force Measurements on the Sr-Bi System	30
2.2.3	Structural Characterization and Meta-Stable Phases	38
2.2.4	Thermal Analysis and Phase Transition Temperatures	45
2.2.5	Comparison with Equilibrium Phase Diagram	48
2.2.6	Summary of the Sr-Bi System	50
2.3 Str	ontium-Antimony Binary System	51
2.3.1	Literature Review	51
2.3.2 Measure	Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) ements	51
2.3.3	Electromotive Force Measurements on the Sr-Sb System	53

2.3	.4	Structural Characterization of the Sr-Sb System	. 59
2.3	.5	Thermal Analysis and Phase Transitions	. 65
2.3	.6	Construction of the Sr-Sb Phase Diagram	. 67
2.3	.7	Summary of the Sr-Sb System	. 69
2.4	Stro	ontium-Tin Binary System	. 70
2.4	.1	Literature Review	. 70
2.4	.2	Electromotive Force Measurements on the Sr-Sn System	. 71
2.4	.3	Structural Characterization of the Sr-Sn System	. 79
2.4	.4	Thermal Analysis and Phase Transitions	. 83
2.4	.5	Verification of the Sr-Sn Phase Diagram	. 85
2.4	.6	Summary of the Sr-Sn System	. 87
2.5	Sun	nmary on the Sr-Bi, Sr-Sb, and Sr-Sn Systems	. 87
Chapter	3.	Electrochemical Deposition into Liquid Metal Electrodes	. 89
3.1	Shi	ft in Redox Potentials in Liquid Metals	. 89
3.2	Eleo	ctrochemical Deposition Cell Design	. 93
3.2	.1	Electrolyte Preparation	. 93
3.2	.2	Electrode Preparation	. 94
3.2	.3	Cell Preparation and Assembly	. 94
3.3	Eleo	ctrochemical Deposition of Sr into Bi	. 95
3.4	Eleo	ctrochemical Deposition of Sr into Sb, Sn	. 98
3.5	Sun	nmary: Deposition into Liquid Bi, Sb, and Sn Metals	. 98
Chapter Technic	4. Jue	Thermodynamic Modeling Using First-Principles Calculations and the CALPHA 100	AD
4.1	Cor	nputational Efforts on the Sr-Sb System	100
4.1	.1	Necessity of Computational Corroboration for the Sr-Sb System	100
4.1	.2	First-principles Calculations	101
4.1	.3	The CALPHAD Technique	104
Chapter	5.	Conclusions and Future Work	110
5.1	Sun	nmary and Conclusions	110
5.2	Fut	ure Work: Removal of Cs from Molten Salts	111
Referen	ces		114

List of Figures

Figure 1.1. Schematic of a simplified electrorefining process, with uranium oxidized from
metallic used nuclear fuel at the anode and pure uranium reduced at the cathode in molten salt
LiCl-KCl-UCl ₃ electrolyte
Figure 1.2. Standard electrode potentials of $M^{z+} M$ vs. the Cl ⁻ /Cl ₂ (g) couple at 600 °C, where z
is the number of electrons in each half-cell reaction and M are the pure metals of fission product
elements [7]
Figure 1.3. Schematic of an electrorefining cell that illustrates the accumulation of Sr and Cs in
the electrolyte due to their more negative redox potentials than U
Figure 1.4. Chemical composition of used nuclear fuel by elemental groups [8]
Figure 1.5. Optical image of the Bi electrode discharged at 50 C g ⁻¹ from BaCl ₂ -LiCl-CaCl ₂ -
NaCl molten salt electrolyte with constant current density (-100 mA cm ⁻²) at 600 °C with
accompanying compositional analysis via EDS [10]7
Figure 1.6. Equilibrium potentials of the Ba, Li, Ca, and Na redox couples at $x_{A(in Bi)} = 0.05$
(triangle) compared to the standard electrode potentials (circle) at 600 °C. Each arrow represents
the shift in potential due to the activity of A in the Bi electrode [10]
Figure 1.7. Electrochemical cell design for reduction of Sr ²⁺ out of LiCl-KCl-SrCl ₂ into a Bi
electrode, simultaneously producing Cl ₂ (g) at an inert anode 10
Figure 1.8. Proposed process for removing Sr and Cs from electrorefiner salts using liquid metal
cathodes, followed by oxidation treatments to develop oxide wasteform
Figure 2.1. Comparison of standard electrode potentials of selected alkali/alkaline-earth
elements calculated using the standard free energies of formation of (a) pure chlorides and (b)
pure fluorides at 873 K [7]
Figure 2.2. XRD patterns (normalized to the most intense peak) of CaF ₂ -SrF ₂ electrolyte before
and after the sintering process, compared with pure CaF ₂ and SrF ₂ diffraction patterns [23] 18
Figure 2.3. Schematic of the electrochemical cell used for electromotive force measurements
from a side view (a) and top view (b), detailing the electrode placement as well as the general
assembly of the system with approximate dimensions
Figure 2.4. Experimental assembly for electromotive force measurements utilizing the
Sr(s) CaF ₂ -SrF ₂ Sr(in M) electrochemical cell
Figure 2.5. Reaction of the pure Sr electrode with the CaF ₂ -SrF ₂ (97-3 mol%) electrolyte
indicated by the darkening of the electrolyte, which leads to the degradation of the
electrochemical cell and irreproducible emf measurements
Figure 2.6. (a) Electromotive force data as a function of time (blue) with temperature (red) for
the electrochemical cell $Sr(s) CaF_2-SrF_2(s) Sr-Bi$ ($x_{Sr} = 0.10$) and (b) emf values as a function of
temperature obtained from the aforementioned electrochemical cell
Figure 2.7. Emf values and temperature measured as a function of time upon cooling and
heating a Sr-Bi $(x_{Sr} = 0.10)$ CaF ₂ -SrF ₂ (s) Sr(in Bi) cell with Sr-Bi alloys $x_{Sr} = 0.10, 0.15$, and
0.20
Figure 2.8. Emf values as a function of temperature upon cooling and heating a Sr-Bi ($x_{Sr} =$
$(0.10) CaF_2-SrF_2(s) Sr(in Bi) cell with Sr-Bi alloys x_{Sr} = 0.10, 0.15, and 0.20.$

Figure 2.9. Graphical representation of E_{cell}/T vs. 1/T to estimate the change in partial molar Figure 2.10. Emf values of various Sr-Bi alloys versus pure Sr, E_{cell} , as a function of temperature **Figure 2.11.** (a) Measured emf values (E_{cell}), (b) natural logarithm of activity in Sr (ln a_{Sr}), and **Figure 2.12.** X-ray diffraction patterns of Sr-Bi alloys (a) $x_{Sr} = 0.05$ to $x_{Sr} = 0.40$ and (b) $x_{Sr} = 0.40$ 0.40 to $x_{Sr} = 0.80$, compared to the diffraction patterns of Sr-Bi intermetallic compounds (*) **Figure 2.13.** Measured XRD patterns of $x_{Sr} = 0.45$ compared to the standard diffraction patterns of Sr-Bi intermetallic compounds, indicating the presence of all three, despite the expected phase **Figure 2.14.** SEM image of $x_{Sr} = 0.25$ alloy that shows the presence of three distinct phases of Bi **Figure 2.15.** Differential scanning calorimetry data collected upon heating Sr-Bi alloys x_{Sr} = 0.05 to $x_{\rm Sr} = 0.30$ at 7 K min⁻¹, indicating phase transitions of eutectic temperatures (I), liquidus Figure 2.16. Comparison of experimentally determined phase behavior with the equilibrium phase diagram, adapted from the work by Wang et al. [16,40]. The phase transition temperatures were determined by emf measurement (\circ) and DSC technique (\Box). The observed phases of Figure 2.17. Emf values of various Sr-Sb alloys versus pure Sr, E_{cell}, as a function of **Figure 2.18.** (a) Measured emf values (E_{cell}), (b) natural log of activity (ln a_{Sr}), and (c) excess Figure 2.19. X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.38$ and **Figure 2.20.** X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.04$ to x_{Sr} = 0.52 and (b) $x_{Sr} = 0.52$ to $x_{Sr} = 0.69$ with standard reference patterns denoted (*) [23,38]...... 64 Figure 2.21. Differential scanning calorimetry data for Sr-Sb compositions (a) $0.03 < x_{Sr} < 0.48$ collected at a scan rate of 20 K min⁻¹, with liquidus transitions indicated by *, the eutectic reaction: Liquid \rightarrow Sb + SrSb₂ (denoted by I), the peritectic reaction: Liquid + Sr₁₁Sb₁₀ \rightarrow SrSb₂ Figure 2.22. Partial Sb-Sr phase diagram developed based on XRD data as well as the transition Figure 2.23. Emf values of various Sr-Sn alloys versus pure Sr, E_{cell}, as a function of **Figure 2.24.** (a) Measured emf values (E_{cell}), (b) natural log of activity (ln a_{Sr}), and (c) excess **Figure 2.25.** X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.05$ to x_{Sr} = 0.30 and (b) $x_{Sr} = 0.40$ to $x_{Sr} = 0.65$ with standard reference patterns denoted (*) [23,38]...... 82 Figure 2.26. Differential scanning calorimetry data for Sr-Sn compositions $0.03 \le x_{Sr} \le 0.35$

Figure 2.27. Sr-Sn phase diagram reproduced from Zhao et al. [59] using CALPHAD modeling
compared with the experimental data from this work
Figure 3.1. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(in Bi)} = 0.05$ to $x_{A(in Bi)}$
= 0.10 compared to the standard electrode potentials (circle) at 500 $^{\circ}$ C [69]. Each arrow
represents the shift in potential due to the activity of A in the Bi electrode
Figure 3.2. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(in Sb)} = 0.05$ to $x_{A(in Sb)}$
= 0.10 compared to the standard electrode potentials (circle) at 650 °C [69]. Each arrow
represents the shift in potential due to the activity of A in the Sb electrode
Figure 3.3. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(in Sn)} = 0.05$ to $x_{A(in Sn)}$
= 0.10 compared to the standard electrode potentials (circle) at 500 °C [69]. Each arrow
represents the shift in potential due to the activity of A in the Sn electrode
Figure 3.4. SEM/EDS images of the Bi electrode following deposition to a specific capacity of
270 C g ⁻¹ at 500 °C in LiCl-KCl-SrCl ₂ (56.7-38.3-5 mol%)
Figure 4.1. The formation energy of the intermetallics as a function of temperature from DFT-
based first-principles calculations, where \Box represent the enthalpies of formation computed via
DFT and the line (convex hull) was determined using CALPHAD modeling 103
Figure 4.2. Comparison of modeled activity of Sr in Sb vs. the activity values determined from
the electromotive force measurements at 988 K 106
Figure 4.3. Computationally constructed Sr-Sb phase diagram using the CALPHAD technique,
based on experimental data from emf/DSC measurements, first-principles calculations, as well as
thermal analysis from Vakhobov et al. [41]

List of Tables

Table 2.1. Measured partial molar entropies and partial molar enthalpies for Sr-Bi alloy
compositions $x_{sr} = 0.05$ to $x_{sr} = 0.75$ as well as linear fits of emf values
Table 2.2. Measured emf, natural log of the activity of Sr in Bi, and the measured excess partial
molar Gibbs energy of strontium of $x_{Sr} = 0.05$ to $x_{Sr} = 0.75$
Table 2.3. Reported crystal structures in Sr-Bi system [29–37]. 39
Table 2.4. Crystal structures identified by XRD pattern analysis at each mole fraction for the Sr-
Bi system
Table 2.5. Summary of transition temperatures determined by emf and DSC techniques. 48
Table 2.6. Comparison of mole fraction, x _{Sr} between as weighed and as measured by ICP-AES.
Table 2.7. Measured partial molar entropies and partial molar enthalpies for Sr-Sb alloy
compositions $x_{Sr} = 0.03$ to $x_{Sr} = 0.69$ as well as linear fits of emf values. Error of the linear fits
are represented by parentheses
Table 2.8. Measured emf, natural log of the activity of Sr in Sb, and the measured excess partial
molar Gibbs energy of strontium for mole fractions $x_{Sr} = 0.03$ to $x_{Sr} = 0.84$
Table 2.9. Reported crystal structures in Sr-Sb system [30,33,45–52]
Table 2.10. Crystal structures identified by XRD pattern analysis at each mole fraction for the
Sr-Sb system
Table 2.11. Summary of liquidus and other transitions as determined by emf and DSC
measurements
Table 2.12. Transitions, type and temperatures seen in the phase diagram in Figure 2.22
Table 2.13. Measured partial molar entropies and partial molar enthalpies for Sr-Sn alloy
compositions $x_{Sr} = 0.03$ to $x_{Sr} = 0.50$ as well as linear fits of emf values. Error of the linear fits
are represented by parentheses
Table 2.14. Measured emf, natural log of the activity of Sr in Sn, and the measured excess
partial molar Gibbs energy of strontium for mole fractions $x_{Sr} = 0.03$ to $x_{Sr} = 0.50$
Table 2.15. Reported crystal structures in Sr-Sn system [30,54,56,57,62–65]
Table 2.16. Crystal structures identified by XRD pattern analysis at each mole fraction for the
Sr-Sn system
Table 2.17. Summary of liquidus and other transitions as determined by emf and DSC
measurements for the Sr-Sn system
Table 3.1. The composition of Bi electrodes after deposition to the specific capacity of 270 C g^{-1}
at 500 °C in eutectic LiCl-KCl electrolyte containing 5 mol% of SrCl ₂ by ICP-AES and the
estimated coulombic efficiency
Table 3.2. The composition of liquid metal electrodes after deposition to the specific capacity of
200 C g ⁻¹ at the specified cell temperatures in eutectic LiCl-KCl electrolyte containing 5 mol%
SrCl ₂ by ICP-AES [76]
Table 4.1. Modeled parameters in SI units for the phases in the Sr-Sb binary system. These
parameters were incorporated with the SGTE data for the pure elements

Table 5.1. The composition of liquid metal electrodes after deposition to the specific capacity	of
100 C g ⁻¹ at the specified cell temperatures in eutectic LiCl-KCl electrolyte containing 5 mol%)
CsCl by ICP-AES 1	112

Acknowledgements

It took a college town to raise this graduate student; and so, I would like to express my heartfelt thanks to the following people, places, and things for their support in this endeavor.

First and foremost, I must extend the majority of my gratitude toward my advisor, Dr. Hojong Kim for going so far as to mentor me as opposed to simply tolerating my existence as most people prefer to do. The stark contrast between my experimental acumen and general scientific ability from 5 years ago and today speaks volumes. Thank you for taking a chance on me; I will do my best throughout my continued career to ensure that it was the right one. Also, a sincere thanks to my committee members Dr. Allison Beese, Dr. Zi-Kui Liu, and Dr. Thomas Mallouk for offering their time and comments.

I would also like to appreciate my fellow group members: Dr. Kuldeep Kumar—you beat me out to be the first graduate from Kim Group, buddy. And I wouldn't have it any other way. So long and thanks for all the whiskey. Work was never the same since you left. Timothy Lichtenstein—for better or worse, we set the tone of this group for the foreseeable future. I'll see you on the other side soon enough. Bees, my friend. Thomas Nigl, Nadia Elbaar, and Jarrod Gesualdi—it's been a pleasure to work alongside all of you. I may never have co-workers as strange again and that makes me sad.

Thank you, as well, to the underappreciated MatSE staff and facilities workers who were also so helpful and courteous to me throughout my time here, even when I deserved to be smacked about for missing deadlines. Eric Sagmuller, Scott Henninger, Peg Yetter, Katina Bartley-Posney, Hayley Colyer, and Mandy Laub—thank you for all you do and all you put up with. Thanks to Mel for keeping everything clean and the kind greetings, even when your Steelers and Penguins were trash like usual and got crushed.

As for my fellow graduate students in arms, thanks for all the game nights, trivia nights, movie nights, and all the other activities that coupled alcohol consumption with a social activity; so my sincerest appreciation to Ethan Kahn, Daniel Schulman, Roger Walker, Lyndsey Denis, Christopher Rotella, Dr. Stephen Weitzner, and Dr. Cassie Marker. To Timothy Pillsbury, thanks for being the best roommate and an amazing friend for the past 9 years or whatever we're at now. A posthumous shout-out to Kildare's Irish Pub for all the good times. F.

To my fellow chemistry TAs, Ciera Wentworth, Gabriella DiDomizio, Kristin DiMonte, and Ryan Myers—thanks for helping me drag myself through this last semester. Teaching is one of the harder aspects of the job I've dealt with here, but y'all made the load a bit lighter by having my back.

A special shout-out to Nicole Orabona for her excellent work on the Ca-Pb system as an undergraduate researcher. You, along with a select few of my lovely CHEM 110 and CHEM 111 students and Millennium Scholars Olivia Vilella and Stephanie (Alex) Brown remind me to watch my back because of how many hard-working and competent undergraduates are right behind me about to compete for the same jobs. All my best.

I would also like to mention Dr. Daniel Esposito, Dr. Jonathan Guyer, and Dr. Theodosia Gougousi for all the opportunities and mentoring they afforded me during my undergraduate career as well as the University of Maryland, Baltimore County (UMBC) and the Meyerhoff Scholars program for shaping my future so significantly and helping me to realize my potential and more so, act on it. Thanks to my family: my mom, Beth Smith; my dad, Douglas Smith; my brother, Steven Smith; and my grandmother, Janet Krout (Grammy) for all of their support and for making me (both literally and in a more metaphorical sense). I love you all very much.

Final thanks go out to my lovely girlfriend, Lourdes Bobbio. You have supported me through thick and thin and I couldn't be more grateful for you. You have made this whole Ph.D. thing much easier for me and I am eternally thankful. I love you very much too.

Words are cheap, but my gratitude truly does run deep. I owe everyone implicitly or explicitly mentioned here a drink. Thanks for everything.

On a professional note, I would like to acknowledge my funding sources. This work was supported by the US Department of Energy Nuclear Engineering University Program (Award No. DE-NE0000113) and the US Department of Energy (Award No. DE-NE0008425), whose views are not necessarily reflected in these findings/conclusions. Thanks for keeping the high purity salts flowing.

Chapter 1. Introduction

1.1 Electrochemical Separation

1.1.1 Nuclear Waste and Electrorefining

As of 2013, the United States has generated over 68,000 metric tons of used nuclear fuel with additions of ~2,000 metric tons per year [1]. Based on the end-of-life for all currently active nuclear reactors in the US, the total amount of nuclear waste is estimated to double [2] and then to further increase as approval has already passed for the Blue Castle Project near Green River, UT with two 1500 MW reactors [3]. Nuclear energy usage in the US has held relatively steady over the past 20 years and is increasing in other countries such as China and India, which makes the management of used nuclear fuel a pressing issue [4]. Currently, used nuclear fuel sits in wet pools near nuclear energy production sites awaiting interment in a permanent geologic repository for tens of thousands of years until radioactivity levels have sufficiently depleted; however, public resistance to the establishment of permanent repositories has resulted in stoppage of the projects (e.g. Yucca Mountain), leaving large amounts of used nuclear fuels trapped onsite in storage only intended to be temporary [5]. Developing recycling methods is one promising approach to mitigate the vast amounts of radioactive waste building up within the US and around the world by separating and re-using uranium from used nuclear fuel [2,6].

One of the most prominently utilized recycling methods is an electrochemical process known as electrorefining. Electrorefining processes used nuclear fuel in order to recover uranium which can then be re-enriched and re-used as nuclear fuel. An electrorefiner system operates as a simple two-electrode electrochemical cell where the used metallic nuclear fuel acts as an anode, an inert steel mandrel as a cathode, and LiCl-KCl-UCl₃ (10 wt%) as a molten salt electrolyte (Figure 1.1).



Figure 1.1. Schematic of a simplified electrorefining process, with uranium oxidized from metallic used nuclear fuel at the anode and pure uranium reduced at the cathode in molten salt LiCl-KCl-UCl₃ electrolyte.

As depicted in Figure 1.1, when current is passed, uranium will be oxidized out of the used fuel anode and pure uranium metal is reduced at the inert steel cathode via the following reactions:

Anode: U(in anode) \rightarrow U³⁺ + 3e⁻

Cathode: $U^{3+} + 3e^- \rightarrow U(\text{on cathode})$

, with the overall reaction given by

U(in anode) \rightarrow U(on cathode)

The recovered pure U can then be subjected to the enrichment process for further re-use. Unfortunately, electrorefiner systems do not operate ideally as shown in Figure 1.1 because used nuclear fuel is composed of diverse fission products (e.g., alkali, alkaline-earth, and rare-earth elements) that possess distinct electrochemical properties including standard reduction potential in the chloride system (Figure 1.2).



Figure 1.2. Standard electrode potentials of $M^{z+}|M$ vs. the Cl⁻/Cl₂ (g) couple at 600 °C, where *z* is the number of electrons in each half-cell reaction and M are the pure metals of fission product elements [7].

A standard reduction potential represents a species' tendency to be reduced, with more positive potentials indicating a higher tendency for reduction. Figure 1.2 depicts the standard reduction potentials of many common components of used nuclear fuel; it is clear that Ba, Sr, K, and Cs are the last elements to reduce out of the LiCl-KCl-UCl₃ electrolyte due to their highly negative potentials and that U, having the most positive potential, is the first element to reduce. At first glance this may not seem to be an issue for the electrorefiner system as U is the element of

interest for recovery from the used nuclear fuel; however, any metallic elements with more negative redox potentials than U (e.g., Cs, Sr, Ba, and rare-earth metals) will be co-oxidized from the anode and accumulated in the molten salt electrolyte (Figure 1.3).



Figure 1.3. Schematic of an electrorefining cell that illustrates the accumulation of Sr and Cs in the electrolyte due to their more negative redox potentials than U.



1.1.2 Challenges with alkali/alkaline-earth fission products in electrorefining



As alkali and alkaline-earth elements (e.g., Sr and Cs) only account for a maximum of 12% of the composition, the figure begs the question of why Sr and Cs are the focus of this work. Firstly, 90 Sr and 137 Cs are dangerous isotopes due to their short half-lives (~30 years), highly ionizing β and γ radiation, and high heat densities (~100 W L⁻¹) [8]. In fact, despite accounting for a small fraction of the composition of used nuclear fuel, Sr and Cs exhibit the highest heat densities among fission products, more than 6 times greater than the other elements of actinides and rare earths. Large quantities of released heat from the radioactive decay of Sr and Cs isotopes may raise the operating temperature of the electrorefiner to unsafe conditions.

Secondly, Sr and Cs are comparatively very difficult to remove from the LiCl-KCl-UCl₃ electrolyte due to their highly negative redox potentials. Based on the redox potentials (Figure 1.2), it is evident that rare earth elements and actinides could theoretically be removed from the

electrolyte by continuing to pass current after all U has been reduced out as they have the next most positive standard reduction potentials. Unfortunately, this same idea cannot be applied to reduce out Sr or Cs as both have standard reduction potentials more negative than Li, a primary component of the molten salt electrolyte. Therefore, any attempt to remove Sr and Cs by simply continuing to reduce elements out of the electrolyte would result in the reduction of Li⁺ to Li, i.e. the decomposition of the main constituent of supporting electrolyte system.

1.1.3 Alkali/Alkaline-Earth Interactions with Liquid Metals

Previous research by Kim et al. [10] suggests that the large electronegativity difference between alkali/alkaline-earth elements and liquid metals such as Bi, Sb, and Pb will allow them to be preferentially separated from molten salt electrolytes. In the case of a multi-component molten salt electrolyte (BaCl₂-LiCl-CaCl₂-NaCl, 16-29-35-20 mol%), Kim et al. [10] found that a liquid metal (Bi) electrode was able to separate conventionally non-separable species. According to the standard reduction potentials for Ba²⁺/Ba (-3.74 V), Li⁺/Li (-3.49 V), Ca²⁺/Ca (-3.44 V), and Na⁺/Na (-3.42 V) vs. Cl⁻/Cl₂(g) at 600 °C, deposition should proceed in the following order: Na \rightarrow Ca \rightarrow Li \rightarrow Ba, with Na being the first to reduce and Ba being the last. However, after discharging the Bi electrode at 50 C g⁻¹ with a constant current density of *j* = -100 mA cm⁻² at 600 °C, Ba was found to be the dominant species in the Bi electrode via post-mortem scanning electron microscopy (SEM) with electron dispersive spectroscopy (EDS) (Figure 1.5).



Figure 1.5. Optical image of the Bi electrode discharged at 50 C g⁻¹ from BaCl₂-LiCl-CaCl₂-NaCl molten salt electrolyte with constant current density (-100 mA cm⁻²) at 600 °C with accompanying compositional analysis via EDS [10].

Despite the conventionally expected deposition order, which had placed Ba as the last species to leave the electrolyte, the solidified electrode was found to be composed of Ba-Ca-Bi intermetallics (35-9-55 mol%). Strong electron donor-acceptor interactions between the elements are believed to cause a shift in their conventional redox potentials which means alkali/alkaline earths can theoretically be selectively deposited into a liquid metal electrode from chloride-based electrolyte. Based on Figure 1.2 and the previous analysis, an inert electrode in a chloride-based salt will be entirely ineffective at removing Sr^{2+} and Cs^+ ; however, an electrode that interacts more strongly with Sr^{2+} and Cs^+ than with Li⁺ or K⁺ could shift the standard reduction potentials unequally, resulting in a different order of reduction as in the BaCl₂-LiCl-CaCl₂-NaCl electrolyte

with the Bi electrode. The effect of the postulated strong atomic interactions between the alkali/alkaline-earth elements and liquid metals can be rationalized using the Nernst equation:

$$E_{\rm eq} = E_{A^{n+}/A}^0 - \frac{RT}{zF} \ln(\frac{a_{\rm A(in\,M)}}{a_{\rm A^{n+}}})$$
(1.1)

where E_{eq} is the equilibrium potential, $E_{A^{n+}/A}^{0}$ is the standard reduction potential of the Aⁿ⁺/A couple, *z* is the number of electrons exchanged in the half reactions (*z* = 2 for alkaline-earth, *z* = 1 for alkali elements), *F* is Faraday's constant (equal to 96485.3 C mol⁻¹), *R* is the ideal gas constant, *T* is the absolute temperature, $a_{A(in M)}$ is the activity of element A in interacting electrode M, and $a_{A^{n+}}$ is the activity of ion Aⁿ⁺ in the electrolyte. Essentially, Eq. 1.1 describes the shift away from the standard reduction potential due to factors such as temperature, and more importantly, activity; as the activity of $a_{A^{n+}}$ in a pure chloride salt is equal to 1, the shift is equivalent to $-\frac{RT}{zF}\ln(a_{A(in M)})$. Therefore, if an electrode choice such as Bi interacts more strongly with Ba²⁺ than Li⁺ or Na⁺ (i.e. lower activity of A in M), the equilibrium potentials for each could be altered and switch the deposition order. Available activity data for Ba²⁺, Li⁺, Ca²⁺, and Na⁺ in Bi was used to estimate the shift in standard reduction potential in the case of the results from Kim et al. (Figure 1.6) [10].



Figure 1.6. Equilibrium potentials of the Ba, Li, Ca, and Na redox couples at $x_{A(in Bi)} = 0.05$ (triangle) compared to the standard electrode potentials (circle) at 600 °C. Each arrow represents the shift in potential due to the activity of A in the Bi electrode [10].

The low activity of Ba in Bi leads to a large shift in equilibrium potential (1.25 V) compared to the next highest shift (0.94 V for Li), which changes the anticipated reduction order to Ba \rightarrow Ca \rightarrow Li \rightarrow Na. If Sr²⁺ and Cs⁺ can be proven to have similarly strong atomic interactions with liquid metals as Ba²⁺, it may be possible to preferentially remove them from the contaminated electrorefiner salts without causing the decomposition of the electrolyte.

1.1.4 Application to Purification of Electrorefiner Molten Salts

Based on the aforementioned ability of Bi to preferentially remove Ba^{2+} from a molten chloride electrolyte containing Li⁺, liquid metal electrodes are a promising option for removing Sr^{2+} and Cs^+ from contaminated LiCl-KCl electrorefiner salt. By leveraging the strong interactions between liquid metals (Bi, Sb, Sn, Pb) and alkali/alkaline-earths (Sr and Cs), it would be possible to selectively deposit Sr^{2+} and Cs^+ out of LiCl-KCl-based electrolytes using an electrochemical cell as depicted in Figure 1.7.



Figure 1.7. Electrochemical cell design for reduction of Sr^{2+} out of LiCl-KCl-SrCl₂ into a Bi electrode, simultaneously producing $Cl_2(g)$ at an inert anode.

By applying a constant current density between the liquid metal working electrode (Bi, in Figure 1.8) and an inert counter electrode, Sr^{2+} ions in the molten salt electrolyte will be reduced into the Bi and removed from the salt via the following reactions:

Anode: $2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$ Cathode: $Sr^{2+} + 2e^{-} \rightarrow Sr(in Bi)$

Selectively removing Sr and Cs from contaminated electrorefiner molten salt electrolytes by leveraging the strong atomic interactions between liquid metals and alkali/alkaline-earth elements will reduce the volume of nuclear waste relegated to permanent storage by allowing for extended use of the electrolyte instead of frequent disposal. Recovery of the Sr and Cs in a liquid metal electrode will allow for them to later be separated as oxides (CsO-SrO₂) through an oxidation treatment for long-term storage as ceramic or glass waste forms, but at a much lower volume than disposing of the entire LiCl-KCl-UCl₃ electrolyte (Figure 1.8).



Figure 1.8. Proposed process for removing Sr and Cs from electrorefiner salts using liquid metal cathodes, followed by oxidation treatments to develop oxide wasteform.

1.2 Dissertation Overview

This dissertation focuses on acquiring fundamental thermodynamic data on alkali/alkalineearth binary systems (Sr-Bi, Sr-Sb, Sr-Sn) to evaluate the effectiveness of various liquid metals at removing Sr^{2+} from LiCl-KCl-based electrolytes as well as attempting to deposit Sr to corroborate with the predicted behavior.

The dissertation is arranged in the following chapters:

In Chapter 2, fundamental thermodynamic properties, including activities, partial molar entropies, and partial molar enthalpies are determined for the Sr-Bi, Sr-Sb, and Sr-Sn binary systems using the electromotive force method to assess the ability of each of the liquid metals to remove Sr^{2+} from electrolyte. Characterization using X-ray diffraction, scanning electron microscopy, and differential scanning calorimetry on each of the systems was also employed to elucidate their phase behavior, often leading to refinement of existing phase diagrams with experimentally-verified properties in this work.

In Chapter 3, the liquid metal electrodes are employed to remove Sr^{2+} from LiCl-KCl-SrCl₂. Compositions of the liquid metal electrodes post-deposition are analyzed using SEM-EDS as well as inductively coupled plasma atomic emission spectroscopy (ICP-AES) to assess the amount of Sr^{2+} removed from the electrolyte. Results are analyzed with respect to predicted behaviors from the electromotive force measurements in Chapter 2.

In Chapter 4, computational efforts using density functional theory (DFT) and the CALPHAD technique to corroborate experimental results are discussed for the case of the Sr-Sb system.

In Chapter 5, the results of the dissertation are summarized and future research directions involving the removal of Cs^+ from molten salt electrolytes are discussed.

Chapter 2. Determination of Fundamental Thermodynamic Properties for Sr-M Binary Systems

2.1 Electromotive Force Method

In order to assess the viability of various liquid metal electrodes for removing alkali/alkaline-earths, thermodynamic data including activity are necessary as the strength of the atomic interactions and therefore the shifts in reduction potentials depend on these properties. Activity data for Sr-M systems (where M = Bi, Sb, Sn) is sparse or absent in available literature and many of the accepted phase diagrams are incomplete or contain unstable phases [11,12]. To gain a more complete understanding and provide valuable fundamental thermodynamic data on these binary systems, electromotive force measurements were conducted [13].

The electromotive force method is an elegant approach to measure partial Gibbs energies using a galvanic cell with no external current flowing, relying on the notion that the amount of work necessary to transfer one mole of an element in valence state z from its pure state into a solution or compound is related to the transfer of charge by:

$$\Delta G = -zFE \tag{2.1}$$

, where *E* is the electromotive force produced by the cell [14,15]. In order to accurately measure the electromotive force between Sr(s) and Sr-M alloys, the following electrochemical cell was devised:

$$Sr(s)|CaF_2-SrF_2|Sr(in M)$$
(2.2)

, where pure strontium acts as the reference electrode (RE), solid CaF_2 -SrF₂ (97-3 mol%) as the electrolyte, and Sr-M alloys as working electrodes (WE). In this electrochemical cell, the half-cell reactions are:

WE:
$$Sr^{2+} + 2e^{-} = Sr(in M)$$
 (2.3)
RE: $Sr^{2+} + 2e^{-} = Sr(s)$

, and the overall cell reaction is:

$$Sr(s) = Sr(in M)$$
(2.4)

The change in partial molar Gibbs energy of strontium, $\Delta \bar{G}_{sr}$, for this reaction is given by:

$$\Delta \bar{G}_{\rm Sr} = \bar{G}_{\rm Sr(in M)} - G_{\rm Sr(s)}^0 = RT \ln(a_{\rm Sr})$$
(2.5)

, where $\bar{G}_{Sr(in M)}$ is the partial molar Gibbs energy of Sr in liquid metal M and $G^0_{Sr(s)}$ is the chemical potential of pure Sr. By applying the Nernst equation to Eq. (1.1), the change in partial molar Gibbs energy of strontium in a given M (and thus activity) is directly related to the cell emf, *E*:

$$E = -\frac{\Delta \bar{G}_{\rm Sr}}{zF} = -\frac{RT}{zF} \ln(a_{\rm Sr(in\,M)})$$
(2.6)

2.1.1 Electrolyte Selection

One of the most difficult aspects of designing an electrochemical system is the choice of electrolyte; CaF₂-SrF₂ (97-3 mol%) was selected because it satisfies several necessary conditions for a reliable electrolyte [14]:

• Electrolyte choice must provide purely ionic conductivity in the temperature range of cell operation

• Any side reactions between the electrodes and electrolyte must be avoided

Constructing an electrochemical cell to effectively meet these requirements for Sr-M alloys is technically challenging due to (i) the high reactivity of pure Sr as well as Sr-M alloys which can degrade the electrolytes or cell components during emf measurements, and (ii) the high melting temperatures of pure Sr ($T_{m, Sr} = 1042$ K) [16] and Sr-M alloys. The solid-state CaF₂ is well known to have substantial ionic conductivity (1.5×10^{-3} S cm⁻¹ at 1073 K) [17,18], suitable for emf measurements. In recent studies, solid-state CaF₂ electrolyte has been utilized in determining the thermodynamic properties of Ca-Bi, Ca-Sb, and Ca-Mg alloys at 723–1100 K [19–21], employing the high stability of CaF₂ electrolyte in emf measurements of calcium alloys. Delcet and Egan [22] also determined the emf values of Ca-Ag and Ca-In alloys using single-crystal CaF₂ at 1073 K via coulometric titration techniques and derived thermodynamic activity values of calcium.

The investigation of Sr-M alloys required using CaF₂-SrF₂ (97-3 mol%) instead of the pure CaF₂ electrolyte to account for the change in electroactive species. According to the analysis of standard electrode potentials in the fluoride system at 873 K (Figure 2.1a), CaF₂ is more stable than SrF₂ and thus, strontium ions are expected to be the most electroactive species in the CaF₂-SrF₂ binary electrolyte. In contrast, SrCl₂ is more stable than CaCl₂ in the chloride system (Figure 2.1b); therefore, calcium becomes the most electroactive species, invalidating the stable emf measurements of Sr-based alloys in CaCl₂-SrCl₂ electrolyte due to side reactions (e.g., Sr + CaCl₂ = SrCl₂ + Ca, $\Delta_r G = -28.9$ kJ at 873 K).



Figure 2.1. Comparison of standard electrode potentials of selected alkali/alkaline-earth elements calculated using the standard free energies of formation of (a) pure chlorides and (b) pure fluorides at 873 K [7].

Solid CaF_2 -SrF₂ (97-3 mol%) electrolyte was prepared by ball-milling 350 g of high-purity CaF_2 (Alfa Aesar, Stock No. 11055), 17.4 g of high-purity SrF₂ (Sigma Aldrich, Stock No. 450030), and 25 g of polyvinyl alcohol binder (Sigma Aldrich, Stock No. 341584) in isopropanol for 24 h. The mixture was dried in air for 24 h and approximately 130 g of powder was taken and

uniaxially pressed at 30 MPa into a pellet 75 mm \times 17 mm in diameter and thickness. Seven wells (each with 11.2 mm \times 12 mm in diameter and depth) were drilled into the pellet with one well in the center and six wells evenly spaced 25.4 mm away from the center (Figure 2.2).

Similarly, seven caps were fabricated from 4 g of the mixture (19 mm \times 10 mm in diameter and height) with a 1.1 mm hole drilled through the center. These green pellets were then fired in air at 393 K for 12 h to remove moisture, 823 K for 12 h to burn away the polyvinyl alcohol binder, and 1273 K for 3 h to sinter. The sintered CaF₂-SrF₂ electrolyte was confirmed to have formed a single-phase solid solution (fluorite phase) by an X-ray diffractometer as shown in Figure 2.2.



Figure 2.2. XRD patterns (normalized to the most intense peak) of CaF_2 -SrF₂ electrolyte before and after the sintering process, compared with pure CaF_2 and SrF₂ diffraction patterns [23].

2.1.2 Electrode Fabrication

Sr-M alloys were selected as working electrodes (WEs) in this electrochemical cell as the reactions of interest (reaction given by: $Sr^{2+} + 2e^- = Sr(in M)$), take place at the Sr-M alloy electrode. Pure Sr(s) was employed as the reference electrode (RE) to measure the activity, i.e. deviation from ideality, created by the liquid metal addition in the working electrodes (reaction given by: $Sr^{2+} + 2e^- = Sr(s)$).

Sr-M alloys at specific compositions were fabricated from strontium ingot (99.5%, Sigma Aldrich) and either bismuth pieces (99.999%, Sigma Aldrich), antimony pieces (99.999%, Alfa Aesar), or tin pieces (99.9999%, Alfa Aesar) using an arc melter (MAM1, Edmund Buhler GmbH) under argon atmosphere. The alloys were machined into a cylindrical shape (10 mm \times 7 mm in diameter and thickness) with a 1.1 mm center hole for insertion of the tungsten electrical lead wire (99.95%, Thermo Shield 1 mm diameter). A schematic of the electrochemical cell is depicted below in Figure 2.3.



Figure 2.3. Schematic of the electrochemical cell used for electromotive force measurements from a side view (a) and top view (b), detailing the electrode placement as well as the general assembly of the system with approximate dimensions.

2.1.3 Electrochemical Cell Assembly

Final assembly of the electrochemical cell was performed in a glovebox under an inert argon environment (O₂ concentration < 0.5 ppm) to mitigate the rapid oxidation of Sr and Sr-M

alloys. The CaF₂-SrF₂ electrolyte was placed in an alumina crucible (8.2 cm diameter \times 3.0 cm height) and tungsten wires (1 mm \times 46 cm in diameter and length) were inserted into alumina tube sheaths, sealed at the top with epoxy, passed through the stainless steel test chamber, through the CaF₂-SrF₂ caps, and into the electrodes (Figure 2.4). The caps were installed to minimize the contamination of alloys during the measurements by physically blocking the vapor-phase transport of strontium.



Figure 2.4. Experimental assembly for electromotive force measurements utilizing the $Sr(s)|CaF_2-SrF_2|Sr(in M)$ electrochemical cell.

2.1.4 Electromotive Force Measurements

The test chamber was then sealed, removed from the glovebox, loaded into a crucible furnace, and evacuated to ~1 Pa. The test chamber was heated at 373 K for 12 h, at 543 K for 12

h under vacuum to remove residual moisture and oxygen, purged three times with high purity argon, and finally heated to 1023 K under flowing argon (~10 mL min⁻¹) atmosphere to melt the electrodes and establish electrical contact with the tungsten wires.

Emf measurements were performed by measuring the potential difference between the reference electrode and each working electrode (Sr-M alloys) sequentially in 180 s intervals during thermal cycles using a potentiostat-galvanostat (Autolab PGSTAT302N, Metrohm AG). Emf data were collected throughout a cooling and reheating cycle between 1113 K and 728 K in 25 K increments. The cell temperature was held constant at each increment for 1.5 h to reach thermal and electrochemical equilibria and ramped at ± 5 K min⁻¹ between increments. The cell temperature was measured using a thermocouple (ASTM type-K) located at the center of the electrolyte, and thermocouple data acquisition system (NI 9211, National Instruments).

2.1.5 Calibration of the $x_{Sr} = 0.10$ Reference Electrode

The use of pure strontium metal as reference electrode caused gradual degradation of the solid-state CaF₂-SrF₂ electrolyte, resulting in irreproducible emf values of Sr alloys during thermal cycles (Figure 2.5).


Figure 2.5. Reaction of the pure Sr electrode with the CaF₂-SrF₂ (97-3 mol%) electrolyte indicated by the darkening of the electrolyte, which leads to the degradation of the electrochemical cell and irreproducible emf measurements.

Instead, a less reactive Sr-Bi alloy ($x_{Sr} = 0.10$) was employed as the reference electrode in emf measurements of various alloy compositions in a manner similar to Newhouse et al. [21]. The choice of the Sr-Bi alloy $x_{Sr} = 0.10$ was advantageous because this alloy composition (1) experiences no phase changes at 700–1100 K, resulting in a linear thermal emf (dE_{cell}/dT); (2) produced highly reproducible emf values for various Sr-Bi alloys during the thermal cycle; and (3) the potential difference between identical $x_{Sr} = 0.10$ electrodes remained less than ±5 mV throughout the emf measurements, implying an excellent stability as a reference electrode. In separate, initial experiments, the electrode potential of the Sr-Bi alloy $x_{Sr} = 0.10$ was determined against pure Sr using a Sr(s)|CaF₂-SrF₂|Sr-Bi($x_{Sr} = 0.10$) cell (Figure 2.6a). By performing several measurements with shorter hold times at each increment (1 h) and only one heating/cooling cycle, the pure Sr electrode reactivity was minimized and a reliable calibration curve was obtained. Using the linear fit of this measurement at $x_{Sr} = 0.10$ (Figure 2.6b), the emf values of Sr-M alloys E_{cell} are reported versus to pure Sr metal:

$$E_{\rm RE} = 6.9 \times 10^{-5} \,\mathrm{T} + 0.922 \,\mathrm{[V]}$$
 vs. pure Sr (2.7)

, which allows the measured emf between the Sr-Bi ($x_{Sr} = 0.10$) reference electrode and the Sr-M working electrodes to be directly related to the emf between the Sr-M working electrodes and pure Sr:

$$E = E_{\text{cell}} + E_{\text{RE}} \tag{2.8}$$





Figure 2.6. (a) Electromotive force data as a function of time (blue) with temperature (red) for the electrochemical cell $Sr(s)|CaF_2-SrF_2(s)|Sr-Bi$ ($x_{Sr} = 0.10$) and (b) emf values as a function of temperature obtained from the aforementioned electrochemical cell.

2.1.6 Calculation of Thermodynamic Properties ($\Delta \bar{S}_{Sr}, \Delta \bar{H}_{Sr}, \ln(a_{Sr}), \bar{G}_{Sr}^{E}$)

Electromotive force data can be used to calculate fundamental thermodynamic properties including activity, partial molar entropy, partial molar enthalpy, and partial molar excess Gibbs energy. In order to demonstrate, emf data from the Sr-Bi system ($x_{Sr} = 0.10, 0.15, and 0.20$) will be used as an example. The emf data as function of time is presented below in Figure 2.7 and is re-plotted as a function of temperature in Figure 2.8.



Figure 2.7. Emf values and temperature measured as a function of time upon cooling and heating a Sr-Bi ($x_{Sr} = 0.10$)|CaF₂-SrF₂(s)|Sr(in Bi) cell with Sr-Bi alloys $x_{Sr} = 0.10$, 0.15, and 0.20.



Figure 2.8. Emf values as a function of temperature upon cooling and heating a Sr-Bi ($x_{Sr} = 0.10$)|CaF₂-SrF₂(s)|Sr(in Bi) cell with Sr-Bi alloys $x_{Sr} = 0.10$, 0.15, and 0.20.

The change in the partial molar entropy of strontium, $\Delta \bar{S}_{Sr}$, is calculated from linear fits of the measured emf data in Figure 2.8 using the following thermodynamic relation, where $\left(\frac{\partial E}{\partial T}\right)_P$ is the slope of the fits:

$$\Delta \bar{S}_{\rm Sr} = -\left(\frac{\partial \Delta \bar{G}_{\rm Sr}}{\partial T}\right)_P = zF\left(\frac{\partial E}{\partial T}\right)_P \tag{2.9}$$

By re-plotting the emf data again as E_{cell}/T vs. 1/T (Figure 2.9), the partial molar enthalpy of

strontium, $\Delta \overline{H}_{Sr}$, can be determined using the Gibbs-Helmholtz relation:

$$\Delta \overline{H}_{\rm Sr} = -T^2 \left(\frac{\partial (\Delta \overline{G}_{\rm Sr}/T)}{\partial T} \right)_P = zFT^2 \left(\frac{\partial (E/T)}{\partial T} \right)_P = zF \frac{\partial (E/T)}{\partial (1/T)}$$
(2.10)



Figure 2.9. Graphical representation of E_{cell}/T vs. 1/T to estimate the change in partial molar enthalpy of alloys $x_{Sr} = 0.10-0.20$, where the slope is $-\Delta \overline{H}_{Sr}/zF$.

Using the Nernst equation, the activity of Sr can be calculated for any specific temperature using the emf values:

$$\ln(a_{Sr}) = -\frac{zFE_{cell}}{RT}$$
(2.11)

The excess partial molar Gibbs energy of Sr, \bar{G}_{Sr}^{E} , can then calculated from the activity data:

$$\bar{G}_{\rm Sr}^{\rm E} = RT \ln \gamma_{\rm Sr} = RT (\ln a_{\rm Sr} - \ln x_{\rm Sr})$$
(2.12)

, where γ_{Sr} is the activity coefficient.

Emf measurements recorded as a function of temperature provide a wealth of thermodynamic data, which allows for a more complete understanding of the capability of each liquid metal (Bi, Sb, Sn) to separate Sr from molten salt electrolytes.

2.2 Strontium-Bismuth Binary System

2.2.1 Literature Review of Sr-Bi

The Sr-Bi phase diagram has been investigated by a number of researchers: Shukarev et al. (1956) [24] constructed the first full Sr-Bi phase diagram using thermal analysis and microscopy, indicating the presence of the SrBi₃, SrBi, Sr₃Bi₂, and Sr₂Bi compounds; Pleasance (1959) [25] followed this work up by performing thermal analysis between $x_{Sr} = 0.00$ and $x_{Sr} = 0.25$, confirming the [Liquid = Bi + SrBi₃] reaction also predicted by Shukarev et al.; Schweitzer and Weeks (1961) [26] clarified liquidus measurements up to $x_{Sr} = 0.10$; and finally, Zhuravlev and Smirnova (1966) [27] performed thermal analysis and microscopy up to $x_{Sr} = 0.45$, concurring with the previous work except in the identification of a polymorphic [α Sr₃Bi₂ = β Sr₃Bi₂] reaction. Despite the amassed body of work on the Sr-Bi system, no available literature contains crystal structure data for the SrBi or Sr₃Bi₂ phases, indicating potential flaws in the descriptions provided by experimental data. A revised phase diagram was recently developed by Wang et al. (2013) [16] using the ThermoCalc software and first-principles calculations, which determined the SrBi and Sr₃Bi₂ phases to be unstable, replacing them with the Sr₁IBi₁₀ and Sr₅Bi₃ phases. While this work

provides a more reasonable phase description of the Sr-Bi system based on the available crystal structure data, thermodynamic data (i.e. activity data) remains unavailable; Wang et al. [16] bemoan this issue themselves, citing the only activity data existent from Klebanov et al. (1986) [28] and their work at 900 K using electromotive force measurements up to $x_{Sr} = 0.17$. However, this data was dismissed by Wang et al. [16] as the "reported activity coefficients are rather scattered" and therefore neglected it from their modeling. Overall, the available phase descriptions for the Sr-Bi system are conflicting and the only source of activity data is unreliable, necessitating further measurement of thermodynamic properties and confirmation of phase behavior to adequately analyze the interactions between Sr and Bi.

2.2.2 Electromotive Force Measurements on the Sr-Bi System

The variation of emf with temperature and composition for Sr-Bi alloys ($x_{Sr} = 0.05-0.75$) is displayed in Figure 2.10a-c, obtained upon cooling and reheating the electrochemical cells between 1023 and 748 K [13]. In general, the emf values were in close agreement between the cooling and heating with less than a 5 mV difference up to $x_{Sr} = 0.30$. In Figure 2.10a, the emf varies linearly with respect to temperature and increases as x_{Sr} decreases above the liquidus [L = L + SrBi₃(s)]; below the liquidus line, the emf does not change with composition and the emf values collapse onto the same line. This is because the emf values are analogous to activity and activity is constant with respect to composition in a two-phase region. In Figure 2.10b, mole fraction $x_{Sr} = 0.30$ exhibits two phase transitions, a liquidus [L = L + Sr₂Bi₃] at 908 K and a solidus [L + Sr₂Bi₃ = SrBi₃ + Sr₂Bi₃] at 843 K.

Emf values of alloys with high strontium content ($0.35 \le x_{Sr} \le 0.75$) exhibited increased hysteresis between the heating-cooling cycles up to a 25 mV difference possibly due to the increased reactivity. For this reason, emf data for high Sr alloys ($x_{Sr} \ge 0.35$) were collected from the first cooling cycle only (Figure 2.10b-c). Mole fraction $x_{Sr} = 0.45$ exhibited a solidus transition [L + Sr₁₁Bi₁₀ = Sr₂Bi₃ + Sr₁₁Bi₁₀] at 908 K (Figure 2.10b); mole fraction $x_{Sr} = 0.55$ exhibited a solidus phase transition [L + Sr₄Bi₃ = Sr₁₁Bi₁₀ + Sr₄Bi₃] at ~985 K (Figure 2.10c). The transition reactions were inferred based on the observed crystal structures at each composition, which will be discussed later in section 2.2.3. It should be noted that the observed crystal structures of the Sr₂Bi₃ and Sr₄Bi₃ phases are well reported in the database, but not included in the most recent Sr-Bi equilibrium phase diagrams.







Figure 2.10. Emf values of various Sr-Bi alloys versus pure Sr, E_{cell} , as a function of temperature for (a) $x_{Sr} = 0.05$ to $x_{Sr} = 0.25$, (b) $x_{Sr} = 0.25$ to $x_{Sr} = 0.55$, and (c) $x_{Sr} = 0.55$ to $x_{Sr} = 0.75$.

The change in the partial molar entropy of strontium, $\Delta \bar{S}_{Sr}$, was calculated from linear fits of the measured emf data in Figure 2.10a-c (Equation 2.9). Similarly, the change in the partial molar enthalpy, $\Delta \bar{H}_{Sr}$, was calculated using the Gibbs-Helmholtz relation (Equation 2.10). As shown in Figure 2.9 for alloys $x_{Sr} = 0.05-0.15$, the change in partial molar enthalpy was estimated based on the slopes by plotting E_{cell}/T versus 1/*T*. The estimated partial molar quantities as well as the linear fits of temperature-dependent emf values are summarized in Table 2.1.

X _{Sr}	<i>T</i> (K)	$\partial E_{\text{cell}} / \partial T (\mu \mathrm{V} \mathrm{K}^{-1})$	$\partial (E_{\text{cell}}/T)/\partial (1/T) \text{ (mV)}$	$\Delta \bar{S}_{Sr}$ (J mol ⁻¹ K ⁻¹)	$\Delta \overline{H}_{Sr}$ (kJ mol ⁻¹)
0.05	728-1007	157	883	30.3	-170.4
0.10	754-1009	69.2	919	13.4	-177.3
0.15	786-987	27.7	926	5.3	-178.7
0.20	835-987	6.4	913	1.2	-176.2
0.20	786-835	-570	1395	-110	-269.2
0.25	883-959	0.8	914	0.2	-176.4
0.25	782-883	-602	1469	-116	-283.5
0.30	908-984	-40.7	904	-7.9	-174.4
0.30	831-908	-611	1423	-118	-274.6
0.30	782-831	-133	1023	-25.7	-197.4
0.35	959-1010	-76.6	964	-14.8	-186.0
0.35	831-959	-527	1327	-101.7	-256.1
0.35	780-831	-181	1039	-34.9	-200.5
0.40	867-1010	-508	926	-98	-178.7
0.40	780-867	-62	1324	-12	-255.5
0.45	959-1010	-519	1197	-100.2	-231.0
0.45	780-959	-94.7	928	-18.3	-179.1
0.50	983-1009	-292	1111	-56.3	-214.4
0.50	779-983	-108	931	-20.8	-179.7
0.55	984-1009	-346	1167	-66.8	-225.2
0.55	779-984	-100	925	-19.3	-178.5
0.65	804-1007	-422	1169	-81.4	-225.6
0.75	933-1009	-2200	2725	-424.5	-525.8
0.75	830-933	-676	1265	-130.4	-244.1

Table 2.1. Measured partial molar entropies and partial molar enthalpies for Sr-Bi alloy compositions $x_{Sr} = 0.05$ to $x_{Sr} = 0.75$ as well as linear fits of emf values.

Using the Nernst equation (Equation 2.11), the activity of Sr in Bi, a_{Sr} , was calculated for specific temperatures of 788 K, 888 K, and 988 K using the measured emf values. The excess partial molar Gibbs energy of Sr, \bar{G}_{Sr}^{E} , was then calculated from the activity data (Equation 2.12). The results of emf values, natural log of the activity, and the excess partial molar Gibbs energy are summarized in Table 2.2 and are presented graphically in Figure 2.11a–c at 888 K.

ra	<i>E</i> (V)			$\ln a_{\rm Sr}$			$\bar{G}_{\rm Sr}^{\rm E}$ (kJ mol ⁻¹)		
ASI	788 K	888 K	988 K	788 K	888 K	988 K	788 K	888 K	988 K
0.05	1.008	1.024	1.039	-29.7	-26.8	-24.4	-175	-176	-176
0.10	0.976	0.982	0.989	-28.7	-25.7	-23.2	-173	-173	-172
0.15	0.948	0.951	0.953	-27.9	-24.9	-22.4	-170	-170	-168
0.20	0.946	0.919	0.920	-27.9	-24.0	-21.6	-172	-165	-164
0.25	0.946	0.891	0.891	-27.9	-23.3	-20.9	-174	-162	-160
0.30	0.919	0.881	0.864	-27.1	-23.0	-20.3	-170	-161	-157
0.35	0.912	0.879	0.838	-26.9	-23.0	-19.7	-169	-162	-153
0.40	0.878	0.880	0.829	-25.9	-23.0	-19.5	-164	-163	-153
0.45	0.879	0.870	0.826	-25.9	-22.7	-19.4	-164	-162	-153
0.50	0.845	0.834	0.822	-24.9	-21.8	-19.3	-159	-156	-153
0.55	0.845	0.835	0.824	-24.9	-21.8	-19.4	-159	-157	-154
0.65	0.843	0.801	0.758	-24.8	-20.9	-17.8	-160	-151	-143
0.75	0.836	0.769	0.610	-24.6	-20.1	-14.3	-159	-146	-115

Table 2.2. Measured emf, natural log of the activity of Sr in Bi, and the measured excess partial molar Gibbs energy of strontium of $x_{Sr} = 0.05$ to $x_{Sr} = 0.75$.







Figure 2.11. (a) Measured emf values (E_{cell}), (b) natural logarithm of activity in Sr (ln a_{Sr}), and (c) excess partial molar Gibbs energy (\bar{G}_{Sr}^{E}) as a function of mole fraction x_{Sr} at 888 K.

Figure 2.11a displays the emf values as a function of strontium mole fraction with the phase compositions of each intermetallic compound as well as liquidus composition at 888 K. In the two-phase region [L+ Sr₂Bi₃] at $0.30 < x_{Sr} < 0.40$, the emf is nearly constant because chemical potential (or activity) of Sr becomes invariant with respect to x_{Sr} in two-phase regions (Figure 2.11a-b). However, in the two-phase region [Sr₂Bi₃ + Sr₁₁Bi₁₀] at $0.40 < x_{Sr} < 0.52$, different emf values were obtained within the same two-phase region, indicating non-equilibrium phase behavior. According to the equilibrium phase diagram, we anticipate that the emf values will approach zero in the two-phase composition domain [Sr₂Bi + Sr] at $x_{Sr} > 0.67$, as observed in the Ca-Bi system

[19]. However, the emf value at $x_{Sr} = 0.75$ remained above 0.75 V versus pure Sr. This discrepancy was due to the formation of meta-stable phases at this composition, comprised of Sr₂Bi, Sr₅Bi₃, and Sr₄Bi₃ without pure Sr phase. In the Sr-Bi system, a large excess partial molar Gibbs energy (as low as -176 kJ mol⁻¹ at $x_{Sr} = 0.05$) was obtained, indicating highly non-ideal solution behavior due to the strong chemical interactions between Sr and Bi (Figure 2.11c).

2.2.3 Structural Characterization and Meta-Stable Phases

Crystal structures of the Sr-Bi alloys were characterized using an X-ray diffractometer (XRD, PANalytical Empryean). Samples were prepared by grinding Sr-Bi alloys into a fine powder using a mortar and pestle in a glovebox under inert argon atmosphere. For equilibrium phase determination, Sr-Bi alloys were annealed at ~15 K below their solidus temperatures for 24 h. The powder samples were coated with mineral oil in order to minimize the oxidation of the alloys during the measurements. A broad amorphous background from mineral oil was present in the XRD patterns at low angles ($10^{\circ} \le 2\theta \le 20^{\circ}$), but was subtracted to facilitate the identification of crystalline phase peaks of Sr-Bi alloys.

Crystal structures of known phases in the Sr-Bi system are summarized in Table 2.3. Xray diffraction patterns for Sr-Bi alloys are presented in Figure 2.12. In general, multiple metastable phases were present in Sr-Bi alloy systems at mole fractions $x_{Sr} \ge 0.25$, which may explain the increased hysteresis in the emf measurements during the cooling-heating cycle as well as unusually high emf values at high strontium concentrations ($x_{Sr} > 0.67$). A summary of observed phases by mole fraction is given in Table 2.4.

Phase	x _{Sr}	Space group	Density	Volume	Lattice param	e parameters	
		(Pearson symbol)	(mg m ⁻³)	(nm ³)	(nm)	(°)	
Bi	0.00	hR6 R-3m	9.81	0.2123	a=0.45459 b=0.45459 c=1.18623	α=90 β=90 γ=120	
SrBi ₃	0.25	cP4 Pm-3m	9.26	0.12818	a=0.5042 b=0.5042 c=0.5042	α=90 β=90 γ=90	
Sr ₂ Bi ₃	0.40	oP20 Pnna	7.6	0.70069	a=1.5631 b=0.6793 c=0.6599	α=90 β=90 γ=90	
Sr ₁₁ Bi ₁₀	0.52	tI84 I4/mmm	6.76	2.9993	a=1.2765 b=1.2765 c=1.8407	α=90 β=90 γ=90	
Sr ₄ Bi ₃	0.57	cI28 I-43d	6.3	1.0306	a=1.0101 b=1.0101 c=1.0101	α=90 β=90 γ=90	
Sr5Bi3	0.63	hP16 P6 ₃ /mcm	5.77	0.61278	a=0.963 b=0.963 c=0.763	α=90 β=90 γ=120	
Sr₂Bi	0.67	tI12 I4/mmm	5.75	0.44377	a=0.501 b=0.501 c=1.768	α=90 β=90 γ=90	
Sr (rt)	1.00	cF4 Fm-3m	2.58	0.2253	a=0.60849 b=0.60849 c=0.60849	α=90 β=90 γ=90	
Sr (ht)	1.00	cI2 Im-3m	2.55	0.1141	a=0.485 b=0.485 c=0.485	α=90 β=90 γ=90	

Table 2.3. Reported crystal structures in Sr-Bi system [29–37].





Figure 2.12. X-ray diffraction patterns of Sr-Bi alloys (a) $x_{Sr} = 0.05$ to $x_{Sr} = 0.40$ and (b) $x_{Sr} = 0.40$ to $x_{Sr} = 0.80$, compared to the diffraction patterns of Sr-Bi intermetallic compounds (*) [23,38].

Table 2.4. Crystal structures identified by XRD pattern analysis at each mole fraction for the Sr-Bi system.

Mole Fraction, <i>x</i> _{Sr}	Phases Observed
0.05, 0.10, 0.15, 0.20	Bi, SrBi ₃
0.25, 0.30, 0.35, 0.40	Bi, SrBi ₃ , Sr ₂ Bi ₃
0.45, 0.50	Bi, Sr_2Bi_3 , $Sr_{11}Bi_{10}$
0.55	$Sr_{11}Bi_{10}$, Sr_4Bi_3
0.60	Sr ₁₁ Bi ₁₀ , Sr ₄ Bi ₃ , Sr ₅ Bi ₃
0.65,0.70, 0.75, 0.80	Sr4Bi3, Sr5Bi3, Sr2Bi

Figure 2.12b indicates the presence of bismuth phase up to $x_{Sr} = 0.40$ although the equilibrium phase diagram predicts its stability only up to $x_{Sr} = 0.25$. Further annealing at ~15 K below the solidus temperature for $x_{Sr} = 0.40$ ($T_{solidus} = 840$ K) was performed to remove the metastable Bi phase, but only a slight reduction in the intensity of Bi phase was observed even after 168 h of annealing, implying that much longer annealing time may be necessary to achieve equilibrium phases. The presence of the Sr₂Bi₃ and Sr₄Bi₃ phases was evident as shown in Figure 2.12a. For instance, mole fraction $x_{Sr} = 0.65$ is expected to be in two-phase equilibrium (Sr₅Bi₃ and Sr₂Bi); however, this alloy composition was found to be comprised of three phases (Sr₅Bi₃, Sr₂Bi, and Sr₄Bi₃) via XRD and SEM/EDS analyses. Similarly, mole fraction $x_{Sr} = 0.45$ is expected to be comprised of 2 phases (Sr₂Bi₃ and Sr₁₁Bi₁₀); however, three phases were identified via XRD (SrBi₃, Sr₂Bi₃, and Sr₁₁Bi₁₀) as shown in Figure 2.13 below.



Figure 2.13. Measured XRD patterns of $x_{Sr} = 0.45$ compared to the standard diffraction patterns of Sr-Bi intermetallic compounds, indicating the presence of all three, despite the expected phase behavior (Sr₂Bi₃ + Sr₁₁Bi₁₀) [23].

Notably absent from the XRD analysis was the presence of pure Sr phase peaks at $x_{Sr} > 0.67$. Mole fractions $x_{Sr} = 0.75$ and $x_{Sr} = 0.80$ were comprised of Sr₂Bi, Sr₄Bi₃ and Sr₅Bi₃ (Figure 2.12b), deviating from the equilibrium phase behavior (Sr₂Bi and Sr). These phase analyses explain the abnormally high emf values > 0.75 V (see Figure 2.10a) as due to the formation of meta-stable phases in emf measurements.

The presence of meta-stable phases at selected compositions was also investigated through microstructural analysis of the Sr-Bi alloys using SEM/EDS. The morphology and microstructure analysis of the annealed alloys was performed using scanning electron microscope (SEM, FEI Quanta 200) fitted with energy dispersive spectroscopy (EDS) capabilities to identify the phases and their compositions. Samples were mounted in epoxy, ground, and polished with emery papers of 100–2000 grit sizes using isopropanol to clean between sandpaper grits.

A back-scattered SEM image obtained from $x_{Sr} = 0.25$ confirmed the formation of three distinct phases of Bi, SrBi₃, and Sr₂Bi₃ based on the chemical analysis by EDS (Figure 2.14). The SEM/EDS results agree the with XRD analysis, although this alloy composition is expected to form a single-phase line compound of SrBi₃. Our structural phase analyses by XRD and SEM/EDS suggest that Sr-Bi alloys exhibit a strong tendency to form various meta-stable phases.



Figure 2.14. SEM image of $x_{Sr} = 0.25$ alloy that shows the presence of three distinct phases of Bi (bright), SrBi₃ (gray), and Sr₂Bi₃ (dark gray) based on chemical analysis by EDS.

2.2.4 Thermal Analysis and Phase Transition Temperatures

Differential scanning calorimetry (DSC) analysis was performed using a thermal analyzer (Netzsch Instruments, STA 449 F3 Jupiter) to detect phase transition temperatures of Sr-Bi alloys to complement the phase behavior determined by the emf techniques. About 20–50 mg of each annealed alloy sample was placed in an alumina crucible with a thin tungsten foil interlayer (4.8 mm diameter \times 0.1 mm thickness) that acted as a reaction barrier between the Sr-Bi alloy and alumina crucible. Thermal analyses were conducted at multiple scan rates (7–20 K min⁻¹) and the

phase transition temperature was determined based on onset temperatures at various scan rates by extrapolating the onset temperatures to the scan rate of 0 K min⁻¹ [39]. The Sr-Bi alloys with $x_{Sr} \ge$ 0.35 were found to damage platinum parts of TG-DSC sensor, possibly due to the vapor phase transport of Sr metal, and were excluded for further measurements. In Figure 2.15, a representative thermmogram is presented at 7 K min⁻¹. At mole fractions up to $x_{Sr} = 0.25$, two major transition temperatures were apparent: one related to the [L + SrBi₃ = Bi + SrBi₃] transition at ~543 (± 2) K and the other to the liquidus [L = L + SrBi₃]. The measured melting temperature of Bi was in excellent agreement with the melting temperature of pure bismuth at 544 K. The liquidus temperatures determined by emf measurements and thermal analysis agree within 7 K.



Figure 2.15. Differential scanning calorimetry data collected upon heating Sr-Bi alloys $x_{Sr} = 0.05$ to $x_{Sr} = 0.30$ at 7 K min⁻¹, indicating phase transitions of eutectic temperatures (I), liquidus temperatures (*), and solidus temperature (II) for $x_{Sr} = 0.30$.

At $x_{Sr} = 0.30$, three transition temperatures were observed: the first at 543 K is related to the melting of meta-stable Bi in accordance with the XRD measurements, the liquidus transition at ~917 K, and the solidus transition at ~843 K. During the solidus transition, the following two reactions are probable: [L + Sr₂Bi₃ = SrBi₃ + Sr₂Bi₃] or [L + Sr₁₁Bi₁₀ = SrBi₃ + Sr₂Bi₃]. The phase transition temperatures determined by thermal analysis and emf measurements are summarized in Table 2.5.

x -	$T_{\rm solidus}({ m K})$	$T_{ m liquidus}$ (K)
ASr	Emf / DSC	Emf / DSC
0.05	— / 543	706 / —
0.10	— / 543	744 / 745
0.15	— / 543	786 / 786
0.20	— / 543	835 / 833
0.25	— / 543	880 / 873
0.30	841 / 843	912 / 917
0.35	843 / —	955 / —
0.40	908 / —	/
0.45	908 / —	/
0.50	979 / —	/
0.55	984 / —	/
0.75	929 / —	/

Table 2.5. Summary of transition temperatures determined by emf and DSC techniques.

2.2.5 Comparison with Equilibrium Phase Diagram

Based on the phase transition temperatures determined by DSC, XRD, and emf measurements, these results were compared with the existing equilibrium phase diagram calculated by Wang et al. (Figure 2.16). The liquidus temperatures of Sr-Bi alloys at mole fractions $x_{Sr} < 0.40$ agreed with our measurements within 10 K. In this work, we identified two additional phases of Sr₂Bi₃, and Sr₄Bi₃ (dashed lines in Figure 2.16) using XRD.



Figure 2.16. Comparison of experimentally determined phase behavior with the equilibrium phase diagram, adapted from the work by Wang et al. [16,40]. The phase transition temperatures were determined by emf measurement (\circ) and DSC technique (\Box). The observed phases of Sr₂Bi₃, and Sr₄Bi₃ are indicated by dashed lines.

At high mole fractions ($x_{Sr} \ge 0.40$), the observed transition temperatures by emf technique deviated substantially from the reported transition temperatures up to 23 K difference. In general,

the discrepancy is primarily due to the non-equilibrium phases present in these Sr-Bi alloys, evidenced by the presence of three phases at these compositions (e.g., Sr_5Bi_3 , Sr_2Bi , and Sr_4Bi_3 at $x_{Sr} = 0.65$) and by the absence of pure Sr phase at $x_{Sr} > 0.67$.

At $x_{Sr} = 0.40$ and 0.45, this work observed a transition at ~906 K while the equilibrium temperature was calculated to be 883 K (~23 K difference). This difference can be explained, in part, by the presence of the Sr₂Bi₃ phase that is not considered in the equilibrium phase diagram calculation and the strong tendency to form non-equilibrium phases. However, Wang et al. [16] attributed this invariant temperature to be the peritectic reaction [L + Sr₅Bi₃ = Sr₁₁Bi₁₀]; Okamoto [12] described this as the allotropic reaction [α Sr₁₁Bi₁₀ = β Sr₁₁Bi₁₀]. These discrepancies invite a scrutiny into the phase behavior of the Sr-Bi system, possibly through advanced computational and careful experimental approaches.

2.2.6 Summary of the Sr-Bi System

This study has determined thermodynamic properties of the binary Sr-Bi system, including activities, partial molar entropies, enthalpies, and excess Gibbs energies. The liquid-state solubility of Sr in Bi was estimated to be ~15 mol% at 788 K and ~40 mol% at 988 K. At high Sr compositions ($x_{Sr} \ge 0.25$), strong non-equilibrium phase behavior was observed; for example, three phases in the binary system and the absent pure Sr phase at $x_{Sr} > 0.67$. In addition, two additional phases of Sr₂Bi₃ and Sr₄Bi₃ were considered in describing the phase behavior of Sr-Bi system, which are not considered in the current Sr-Bi equilibrium phase diagram. Combining the high liquid-state solubility and the strong chemical interactions between Sr and Bi (a_{Sr} as low as 1.2 ×

 10^{-13}), Bi shows promise as an electrode material for separating dissolved strontium ions (Sr²⁺) from molten salt electrolytes (e.g., LiCl-KCl-SrCl₂).

2.3 Strontium-Antimony Binary System

2.3.1 Literature Review

Available literature concerning the Sr-Sb system is sparse. Vakhobov et al. [41] provides the most comprehensive understanding using differential thermal analysis across the full composition range of the phase diagram to identify phase transition temperatures; however, Vakhobov et al.'s identification of the phases present is based on the work of Shukarev et al. (1957) [42]. Shukarev et al. identifies 4 intermetallic compounds: SrSb₃, SrSb, Sr₃Sb₂, and Sr₂Sb; unfortunately, SrSb₃ and SrSb are not present in any crystal structure databases. This leaves the Sr₂Sb and Sr₃Sb₂ phases as the only feasibly existent intermetallic compounds, meaning that the current phase diagram proposed by Vakhobov et al. [41] and refined by Okamoto et al. [11] contains inconsistencies in phase description of Sr-Sb alloys. No activity data is available for the Sr-Sb system either, making it a prime candidate for investigation especially given that Sr and Sb are postulated to have even stronger interactions, i.e. lower activities, than Sr in Bi based on the similar behavior of Ba in Sb [43].

2.3.2 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) Measurements

A large amount of metal vapor was observed during the arc-melting of Sr-Sb alloys for electromotive force measurements, which led to the concern that the Sr-Sb alloys could differ from

the intended compositions. Induction Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Perkin-Elmer Optima 5300DV) was used to verify the compositions of the arc-melted Sr-Sb alloys with a maximum of 4 % error of the measured value. As x_{Sr} increased, so did the discrepancy between the actual composition and the nominal composition likely as a result of increased Sr vaporization during the arc melting process (Table 2.6). Compositions are referred to using their ICP-AES measured values instead of the as-weighed compositions prior to arc-melting.

ction, $x_{\rm Sr}$
Measured (ICP-AES)
0.03
0.04
0.07
0.09
0.14
0.20
0.23
0.30
0.33
0.38
0.43
0.48
0.52
0.57
0.60
0.62
0.69
0.84

Table 2.6. Comparison of mole fraction, x_{Sr} between as weighed and as measured by ICP-AES.

2.3.3 Electromotive Force Measurements on the Sr-Sb System

Using the electrochemical cell Sr-Bi ($x_{Sr} = 0.10$)|CaF₂-SrF₂(s)|Sr(in Sb) and the aforementioned experimental procedure, emf values were recorded over a temperature range of 833-1113 K for 16 Sr-Sb alloy compositions ranging from $x_{Sr} = 0.03$ to $x_{Sr} = 0.84$ [44]. Due to undercooling effects (hysteresis between heating/cooling cycles of > 20 mV), only the heating curves were considered in the analysis, while the cooling cycles were discarded [43]. Electromotive force measurements were plotted as a function of temperature for all measured mole fractions (Figure 2.17a-b).





Figure 2.17. Emf values of various Sr-Sb alloys versus pure Sr, E_{cell} , as a function of temperature for (a) $x_{Sr} = 0.03$ to $x_{Sr} = 0.53$ and (b) $x_{Sr} = 0.43$ to $x_{Sr} = 0.84$.

Emf decreases linearly as a function of temperature above the liquidus, while below the liquidus the activity of Sr is invariant as a function x_{Sr} , as the system enters a two-phase region and the emf values collapse onto the same curve. This is because activity is constant in a two-phase region and emf is directly related to activity via the Nernst equation (Equation 2.11). As such, phase transitions are indicated in the plots by changes in the slope of the emf, i.e. changes in the partial molar entropy (Equation 2.9). At temperatures lower than 875 K, the emf values are less reproducible and more scattered; this is believed to be due decreased ionic conductivity in the electrolyte at lower temperatures as well as worsening contact between the electrolyte and Sr-Sb

alloy electrodes due to the absence of any liquid phase. Higher mole fractions ($x_{Sr} > 0.55$) experienced the least stability with emf variability of up to 50 mV between runs due to increased Sr content in the alloys degrading the electrolyte as well as the high melting temperature of these alloys that prevented intimate contact between the electrode and the electrolyte. Figure 4b shows the effect of transitioning into the SrSb₂ + Sr two-phase region with the $x_{Sr} = 0.84$ alloy, as the presence of pure Sr leads to a dramatic decrease in the emf as the activity of pure Sr is unity. The electromotive force data was used to calculate the change in partial molar entropy ($\Delta \overline{S}_{Sr}$) and partial molar enthalpy ($\Delta \overline{H}_{Sr}$) in linear regions using equations 2.9 and 2.10 (Table 2.7).

Table 2.7. Measured partial molar entropies and partial molar enthalpies for Sr-Sb alloy compositions $x_{Sr} = 0.03$ to $x_{Sr} = 0.69$ as well as linear fits of emf values. Error of the linear fits are represented by parentheses.

<i>x</i> _{Sr}	<i>T</i> (K)	$\partial E / \partial T (\mu V \mathrm{K}^{-1})$	$\partial(E/T)/\partial(1/T)$ (mV)	$\Delta \bar{S}_{Sr} (J \text{ mol}^{-1} \text{ K}^{-1})$	$\Delta \overline{H}_{Sr}$ (kJ mol ⁻¹)	Adj-R ²
0.03	886-1090	174 (4)	1006 (4)	33.6	-194.1	0.996
0.04	888-1092	142 (2)	1017 (2)	27.3	-196.2	0.999
0.07	908-1087	73 (3)	1057 (3)	14.2	-203.9	0.986
0.09	882-1089	66 (2)	1052 (2)	12.7	-202.9	0.994
0.14	908-1087	-1 (4)	1080 (4)	-0.2	-208.4	-0.154
0.20	860-933	-435 (9)	1462 (8)	-83.9	-282.1	0.999
0.20	933-1089	-6 (1)	1062 (1)	-1.1	-205.0	0.764
0.23	928-979	-484 (21)	1510 (20)	-93.4	-291.4	0.996
0.23	979-1082	-38 (2)	1074 (2)	-7.4	-207.3	0.987
0.30	904-1082	-543 (16)	1565 (16)	-104.8	-302.0	0.994
0.33	877-1082	-573 (14)	1596 (14)	-110.6	-308.0	0.995
0.38	833-983	11 (1)	1001 (0)	2.1	-193.1	0.981
0.43	882-1089	-176(8)	1116(8)	-33.9	-215.4	0.984
0.52	884-1087	-162(13)	1099(12)	-31.2	-212.2	0.951
0.57	858-1111	-378 (14)	1248 (14)	-72.8	-240.8	0.987
0.60	908-1111	-400(45)	1221(45)	-77.3	-235.6	0.909
0.62	908-1111	-396(35)	1221(35)	-76.5	-235.6	0.942
0.69	873-1113	-238(13)	1039(13)	-45.9	-200.6	0.971

Using the Nernst equation (Equation 2.11), the activity of Sr in Sb was calculated for each alloy at 888 K, 988 K, and 1088 K and the partial molar excess Gibbs free energy (\bar{G}_{Sr}^{E}) was also calculated using Equation 2.12. The resulting values are listed below in Table 2.8 and are depicted graphically for T = 988 K in Figure 2.18a-c.

Table 2.8. Measured emf, natural log of the activity of Sr in Sb, and the measured excess partial molar Gibbs energy of strontium for mole fractions $x_{Sr} = 0.03$ to $x_{Sr} = 0.84$.

XSr	<i>E</i> (V)			$\ln a_{\rm Sr}$			$ar{G}_{ m Sr}^{ m E}$ (kJ mol ⁻¹)		
	888 K	988 K	1088 K	888 K	988 K	1088 K	888 K	988 K	1088 K
0.03	1.161	1.178	1.195	-30.3	-27.7	-25.5	-197	-197	-197
0.04	1.143	1.157	1.171	-29.9	-27.2	-25.0	-197	-197	-198
0.07	1.122	1.129	1.136	-29.3	-26.5	-24.2	-197	-196	-195
0.09	1.111	1.117	1.124	-29.0	-26.2	-24.0	-196	-196	-195
0.14	1.079	1.079	1.079	-28.2	-25.3	-23.0	-194	-192	-191
0.20	1.075	1.056	1.055	-28.1	-24.8	-22.5	-196	-190	-189
0.23	1.080	1.036	1.033	-28.2	-24.3	-22.0	-198	-188	-186
0.30	1.083	1.029	0.974	-28.3	-24.2	-20.8	-200	-189	-177
0.33	1.087	1.030	0.973	-28.4	-24.2	-20.8	-202	-190	-178
0.38	1.011	1.014	0.968	-26.4	-23.8	-20.7	-188	-188	-178
0.43	0.964	0.941	0.925	-25.2	-22.1	-19.7	-180	-175	-171
0.52	0.959	0.939	0.926	-25.1	-22.1	-19.8	-180	-176	-173
0.57	0.912	0.875	0.837	-23.8	-20.6	-17.9	-172	-164	-157
0.60	0.882	0.816	0.786	-23.1	-19.2	-16.8	-166	-153	-147
0.62	0.880	0.824	0.792	-23.0	-19.4	-16.9	-166	-155	-149
0.69	0.828	0.804	0.780	-21.6	-18.9	-16.6	-157	-152	-147
0.84	0.014	0.014	0.013	-0.4	-0.3	-0.3	-1	-1	-1





Figure 2.18. (a) Measured emf values (E_{cell}), (b) natural log of activity (ln a_{Sr}), and (c) excess molar partial Gibbs energy (\overline{G}_{Sr}^E) as a function of x_{Sr} at 988 K.

Figure 2.18a presents the emf values as a function of Sr mole fraction (x_{Sr}) with the liquidus composition and proposed intermetallic phases superimposed at 988 K. The emf clearly decreases as a function of x_{Sr} until hitting the liquidus composition, at which point the emf becomes essentially constant with respect to x_{Sr} in the two-phase regions; this invariance is a result of the chemical potential of Sr being constant in two-phase regions. Figure 2.18b and Figure 2.18c depict the natural logarithm of activity of Sr in Sb and the partial molar excess Gibbs energy of Sr respectively as functions of x_{Sr} at 988 K. The activity of Sr in Sb in the $x_{Sr} = 0.03$ alloy at 988 K is $a_{Sr} = 9.33 \times 10^{-13}$ with $\bar{G}_{Sr}^{E} = -197$ kJ mol⁻¹ indicating very strong atomic interactions, i.e. non-ideal solution behavior. Also, at mole fraction $x_{Sr} = 0.84$, $\bar{G}_{Sr}^{E} = -1$ kJ mol⁻¹ with an activity of $a_{Sr} = 0.74$;
this is in line with expectation as the emf values drop to nearly zero as a result of the presence of pure Sr.

2.3.4 Structural Characterization of the Sr-Sb System

Crystal structures of the Sr-Sb alloys were characterized using an X-ray diffraction. For equilibrium phase determination, Sr-Sb alloys were annealed at ~15 K below their solidus temperatures (based on transitions from Vakhobov et al. [41]) for 24 h with the exception of x_{Sr} = 0.43 as it reacted with its stainless steel casing when annealing was attempted and thus was measured as-fabricated. Samples were then prepared by grinding Sr-Sb alloys into a fine powder using a mortar and pestle in a glovebox under inert argon atmosphere. The powder samples were coated with mineral oil in order to minimize the oxidation of the alloys during the measurements. A broad amorphous background from mineral oil was present in XRD patterns at low angles (10 ° < 2 θ < 20 °) and was subtracted to facilitate the identification of crystalline phase peaks of Sr-Sb alloys.

Analysis of the acquired XRD patterns identified the SrSb₂, as well as Sr₁₁Sb₁₀, Sr₂Sb₃, Sr₁₆Sb₁₁, Sr₅Sb₃ (hex), and Sr₂Sb phases in the binary system; select compositions ($x_{Sr} = 0.38$ and $x_{Sr} = 0.69$) are depicted in Figure 2.19 below. The reported crystal structures for the observed phases are available in Table 2.9. The absence of the SrSb₃, SrSb, and Sr₃Sb₂ phases is in direct contrast to previously proposed phase diagrams [11,41]. Aside from the significant changes in the phases identified versus previous understanding, there are several items of note: firstly, the Sr₅Sb₃ (hex) structure was found as opposed to the Sr₅Sb₃ (ortho) phase; and secondly, at higher mole fractions ($x_{Sr} > 0.50$) non-equilibrium phases were identified such as Sr₅Sb₃ at $x_{Sr} = 0.69$ where Sr₂Sb + Sr would be the expected phase domain (Figure 2.19b). This is likely due to an inability to anneal away non-equilibrium phases in a 24 h time span as the solid-solid transitions will occur much slower compared to many of the lower temperature liquid-solid transitions, which results in trapping of meta-stable phases following the rapid cooling arc-melting fabrication process.

Phase	<i>x</i> _{Sr}	Space group D	Density Volume		Lattice parameters		
		(Pearson symbol)	(mg m ⁻³)	(nm³)	(nm)	(°)	
Sb	0.00	hR6 R-3m	6.69	0.1812	a=0.43084 b=0.43084 c=1.1274	α=90 β=90 γ=120	
SrSb ₂	0.33	mP6 P12 ₁ /m1	5.85	0.18797	a=0.4887 b=0.428 c=0.94838	α=90 β=108.627 γ=90	
Sr ₂ Sb ₃	0.40	mP40 P12 ₁ /c1	5.46	1.31595	a=0.6670 b=1.2973 c=1.5208	α=90 β=90.09 γ=90	
Sr ₁₁ Sb ₁₀	0.52	tI84 I4/mmm	5.17	2.8021	a=1.2454 b=1.2454 c=1.8066	α=90 β=90 γ=90	
Sr ₁₆ Sb ₁₁	0.59	tP56 P-42 ₁ m	4.61	1.9745	a=1.29341 b=1.29341 c=1.18027	α=90 β=90 γ=90	
Sr ₅ Sb ₃ (hex)	0.63	hP16 P6 ₃ /mcm	4.6	0.57957	a=0.95037 b=0.95037 c=0.95037	α=90 β=90 γ=120	
Sr ₂ Sb	0.67	tI12 I4/mmm	4.53	0.43547	a=0.5002 b=0.5002 c=1.7405	α=90 β=90 γ=90	
Sr (rt)	1.00	cF4 Fm-3m	2.58	0.2253	a=0.60849 b=0.60849 c=0.60849	α=90 β=90 γ=90	

Table 2.9. Reported crystal structures in Sr-Sb system [30,33,45–52].

Sr (ht)	1.00	cI2	2.55	0.1141	a=0.485	α=90
		Im-3m			b=0.485	β=90
					c=0.485	γ=90





Figure 2.19. X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.38$ and (b) $x_{Sr} = 0.69$ with standard reference patterns denoted (*) [23].

X-ray diffraction patterns were also measured for the remainder of the full composition range covered by emf measurements; the patterns are depicted below in Figure 2.20. Phases observed at each mole fraction are listed in Table 2.10.





Figure 2.20. X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.04$ to $x_{Sr} = 0.52$ and (b) $x_{Sr} = 0.52$ to $x_{Sr} = 0.69$ with standard reference patterns denoted (*) [23,38].

Table 2.10. Crystal structures identified by XRD pattern analysis at each mole fraction for the Sr-Sb system.

Mole Fraction, x_{Sr}	Phases Observed
0.04, 0.20	Sb, SrSb ₂
0.33	SrSb ₂
0.38	$SrSb_2$, Sr_2Sb_3 , $Sr_{11}Sb_{10}$
0.52	Sr_2Sb_3 , $Sr_{11}Sb_{10}$
0.57	$Sr_{11}Sb_{10}, Sr_{16}Sb_{11}, Sr_5Sb_3$ (hex)
0.62	$Sr_{16}Sb_{11}$, Sr_5Sb_3 (hex), Sr_2Sb
0.69	Sr ₅ Sb ₃ (hex), Sr ₂ Sb, Sr

2.3.5 Thermal Analysis and Phase Transitions

Differential scanning calorimetry analysis was performed to detect phase transition temperatures of Sr-Sb alloys to complement the phase behavior determined by the emf technique in a similar manner to the method discussed in Chapter 2.2.4. Sr-Sb alloys with $x_{Sr} > 0.20$ began to react with the alumina crucible, possibly due to the vapor phase transport of Sr, and therefore no DSC measurements were performed above compositions of $x_{Sr} = 0.20$.

Thermal analysis was performed using DSC over a temperature range of 725-1050 K at scan rates of 5, 10, 15, and 20 K min⁻¹, with the 20 K min⁻¹ scan depicted for each composition (Figure 2.21). Two major transitions were observed over the composition range, one being the liquidus temperature for several of the tested compositions $[L = L + SrSb_2]$ and the other being the solidus transition to the Sb + SrSb₂ region. For the liquidus measurements, DSC transition temperatures agreed with the emf transition temperatures within 4 K, except for $x_{Sr} = 0.07$, which deviated by 13 K (Table 2.11); however, the larger deviation is likely due to fitting difficulty as a result of overlap with the solidus peak. DSC measurements for the solidus transition were self-consistent within 5 K over all measured compositions.



Figure 2.21. Differential scanning calorimetry data for Sr-Sb compositions (a) $0.03 < x_{Sr} < 0.48$ collected at a scan rate of 20 K min⁻¹, with liquidus transitions indicated by *, the eutectic reaction: Liquid \rightarrow Sb + SrSb₂ (denoted by I), the peritectic reaction: Liquid + Sr₁₁Sb₁₀ \rightarrow SrSb₂ (denoted by II), and the eutectic reaction: Liquid \rightarrow Sr₁₁Sb₁₀ + Sr₂Sb₃ (denoted by III).

$\chi_{ m Sr}$		T _{liquidus} (K)		
	emf/DSC	emf/DSC	emf/DSC	emf/DSC
	Ι	II	III	*
0.03	—/853	/	/	891/887
0.04	—/854	/	/	888/887
0.07	/	/	/	883/—
0.09	—/853	/	/	879/—
0.14	—/849	/	/	890/—
0.20	/854	/	/	933/918
0.23	—/851	/	/	970/977
0.30	—/852	/	/	—/1026
0.33	/848	—/1000	/	—/1077
0.38	/	996/995	/	—/1164
0.43	/	—/993	—/1131	/
0.52	/	/	—/1134	/

 Table 2.11.
 Summary of liquidus and other transitions as determined by emf and DSC measurements.

2.3.6 Construction of the Sr-Sb Phase Diagram

Based on the emf and DSC data, as well as the first principles calculations, CALPHAD modeling was performed to develop the Sr-Sb phase diagram [40]; the use of computational methods to improve understanding of the Sr-Sb system will be discussed in detail in Chapter 4. The resulting phase diagram is depicted below in Figure 2.22.



Figure 2.22. Partial Sb-Sr phase diagram developed based on XRD data as well as the transition temperatures predicted by emf and DSC measurements.

The phase diagram is plotted with the phase boundary results from the emf and DSC measurements from this study and assumes the $Sr_{16}Sb_{11}$, $Sr_{11}Sb_{10}$, Sr_2Sb , Sr_2Sb_3 , Sr_5Sb_3 and $SrSb_2$ phases as stable due to the XRD data. Transition reactions and temperatures estimated using the emf and DSC data are listed in Table 2.12.

Transition	Туре	Temperature (K)
Liquid \rightarrow Rhombohedral + SrSb ₂	Eutectic	840
Liquid + $Sr_{11}Sb_{10} \rightarrow SrSb_2$	Peritectic	996
$SrSb_2 + Sr_{11}Sb_{10} \rightarrow Sr_2Sb_3$	Peritectoid	932
$Liquid + Sr_{16}Sb_{11} \rightarrow Sr_{11}Sb_{10}$	Peritectic	1135

Table 2.12. Transitions, type and temperatures seen in the phase diagram in Figure 2.22

The transition observed by emf at 996 K is reproduced with a peritectic reaction of $[L + Sr_{11}Sb_{10} = SrSb_2]$. The phase diagram and predicted reactions differ significantly from previously proposed phase diagrams, mostly due to the establishment of the stability of the $Sr_{16}Sb_{11}$, $Sr_{11}Sb_{10}$, Sr_2Sb , Sr_2Sb_3 , Sr_5Sb_3 and $SrSb_2$ phases, as well as the rejection of the $SrSb_3$, $SrSb_3$, and Sr_3Sb_2 phases as unstable.

2.3.7 Summary of the Sr-Sb System

This study has determined thermodynamic properties of the binary Sr-Sb system, including activities, partial molar entropies, enthalpies, and excess Gibbs energies; X-ray diffraction measurements determined the presence of the SrSb₂, Sr₂Sb₃, Sr₁₁Sb₁₀, Sr₁₆Sb₁₁, and Sr₅Sb₃ (hex) phases and contradicted the reported presence of the SrSb₃, SrSb, and Sr₃Sb₂ phases in the Sr-Sb phase diagram. Using the emf data, XRD and DSC characterization, and CALPHAD modeling, an improved Sr-Sb phase diagram was developed. The strong atomic interactions between Sr and Sb (a_{Sr} as low as 1.5×10^{-12} at 988 K and $x_{Sr} = 0.04$) indicate promise as an electrode material for separating dissolved strontium ions (Sr²⁺) from molten salt electrolytes (e.g., LiCl-KCl-SrCl₂).

2.4 Strontium-Tin Binary System

2.4.1 Literature Review

In contrast to the Sr-Bi and Sr-Sb systems, the phase behavior of the Sr-Sn system has been thoroughly investigated. Ray (1930) [53] was the first to perform thermal analysis and microscopy, identifying the $SrSn_5$ and $SrSn_3$ phases. No further measurements were performed until 1981, when Widera and Schafer [54] used thermal analysis and XRD to identify SrSn₃, SrSn, Sr₅Sn₃, and Sr_2Sn . In the same year, Marshall and Chang [55] determined that the previously observed $SrSn_5$ phase was in fact SrSn₄. Okamoto and Massalski (1990) [56] developed the first full Sr-Sn phase diagram; however, work by Zurcher (2001) [57] indicated the stability of a newly discovered Sr₃Sn₅ phase. Following this development, the full composition range was re-investigated by Palenzona and Pani (2004) [58] using thermal analysis, optical microscopy, and XRD. Zhao et al. (2012) [59] refined all of the available data from the aforementioned works and applied a hybrid approach using both first-principles calculations and the CALPHAD method to create an improved Sr-Sn phase diagram and calculate the enthalpies of formation for all of the observed intermetallic compounds (SrSn₄, SrSn₃, Sr₃Sn₅, SrSn, Sr₅Sn₃, and Sr₂Sn). Unfortunately, while the phase behavior of the Sr-Sn system is well-assessed, the quantity of thermodynamic data is lacking. Klebanov et al. (1985) [60] determined the activity of Sr in Sn at 627 °C for low Sr compositions; however, this is the extent of the available activity data. In order to assess the viability of a Sn electrode for electrochemical separations, electromotive force measurements need to be performed to fill the void of thermodynamic data.

2.4.2 Electromotive Force Measurements on the Sr-Sn System

Using the electrochemical cell Sr-Bi ($x_{Sr} = 0.10$)|CaF₂-SrF₂(s)|Sr(in Sn) and the aforementioned experimental procedure, emf values were recorded over a temperature range of 730-1108 K for 12 Sr-Sn alloy compositions ranging from $x_{Sr} = 0.03$ to $x_{Sr} = 0.50$ [61]. Data from the heating curves is displayed, although the heating and cooling curves differed by < 5 mV for alloy compositions $x_{Sr} \le 0.30$ and by < 20 mV for alloy compositions $x_{Sr} \ge 0.30$. Emf measurements are presented below in Figure 2.23.





Figure 2.23. Emf values of various Sr-Sn alloys versus pure Sr, E_{cell} , as a function of temperature for (a) $x_{Sr} = 0.03$ to $x_{Sr} = 0.30$ and (b) $x_{Sr} = 0.30$ to $x_{Sr} = 0.50$.

As previously noted for the Sr-Bi and Sr-Sb systems, emf decreases linearly as a function of temperature above the liquidus temperature, while below the liquidus temperature the activity of Sr is invariant as a function x_{Sr} indicating a two-phase region. Mole fractions $0.03 \le x_{Sr} \le 0.10$ remained in the liquid phase over the entirety of the measured temperature range; mole fractions $0.15 \le x_{Sr} \le 0.25$ collapse onto the same line, indicative of the transition [L = L + SrSn₃] (Figure 2.23a). Mole fraction $x_{Sr} = 0.30$ exhibits 2 transitions: the first at 987 K, [L = L + Sr₃Sn₅], and the second at 880 K [L + Sr₃Sn₅ = L + SrSn₃]. The calculated phase diagram from Zhao et al. [59] indicates that the aforementioned transition should be $[L + Sr_3Sn_5 = SrSn_3 + Sr_3Sn_5]$; however, the discrepancy is explained using XRD, indicating the presence of meta-stable Sn at $x_{Sr} = 0.30$ which leads to the observed behavior. Mole fractions $0.30 \le x_{Sr} \le 0.45$ all collapse onto the line represented by L + Sr_3Sn_5. As x_{Sr} increases, the emf continues to decrease as a result of the increased Sr content in the equilibrium compounds (Figure 2.23b). Sr-Sn compositions with $x_{Sr} \ge 0.50$ exhibited unstable emf measurements, likely due to the high melting temperatures of the compounds preventing good contact with the electrolyte as well as increased reaction with the electrolyte due to the higher Sr content. The electromotive force data was used to calculate the change in partial molar entropy ($\Delta \overline{S}_{Sr}$) and partial molar enthalpy ($\Delta \overline{H}_{Sr}$) in linear regions using equations 2.9 and 2.10 (Table 2.13).

Table 2.13. Measured partial molar entropies and partial molar enthalpies for Sr-Sn alloy compositions $x_{Sr} = 0.03$ to $x_{Sr} = 0.50$ as well as linear fits of emf values. Error of the linear fits are represented by parentheses.

X _{Sr}	<i>T</i> (K)	$\partial E / \partial T (\mu V K^{-1})$	$\partial (E/T)/\partial (1/T) (\mathrm{mV})$	$\Delta \bar{S}_{ m Sr}$ (J mol ⁻¹ K ⁻¹)	$\Delta \overline{H}_{Sr}$ (kJ mol ⁻¹)	Adj-R ²
0.03	884-1087	137(2)	744(2)	26	143	0.998
0.05	758-1088	107(0)	758(0)	21	146	0.999
0.08	758-1088	69(1)	759(1)	13	147	0.994
0.10	758-1088	57(1)	757(1)	11	146	0.992
0.15	754-1107	21(1)	757(1)	4	146	0.958
0.15	728-754	-264	973	-51	188	N/A
0.20	834-1112	-17(1)	736(1)	-3	142	0.947
0.20	757-834	-477(30)	1122(24)	-92	217	0.988
0.25	880-1106	-39(3)	724(3)	-8	140	0.939
0.25	728-880	-607(46)	1230(37)	-117	237	0.967
0.30	982-1106	-81(10)	709(11)	-16	137	0.925
0.30	881-982	-459(11)	1081(11)	-89	209	0.998
0.30	729-881	-649(39)	1256(32)	-125	242	0.979
0.35	1057-1106	-305(49)	907(54)	-59	175	0.949
0.35	855-1057	-534(15)	1153(15)	-103	222	0.993
0.35	754-855	-207(45)	880(37)	-40	170	0.832
0.40	1084-1108	-177	752	-34	145	N/A
0.40	859-1084	-542(21)	1154(21)	-105	223	0.987
0.40	732-859	-138(27)	799(21)	-27	154	0.867
0.45	855-1083	-550(24)	1163(24)	-106	224	0.983
0.45	730-855	-246(19)	893(15)	-47	172	0.971

Using the Nernst equation (Equation 2.11), the activity of Sr in Sn was calculated for each alloy at 850 K, 950 K, and 1050 K and the partial molar excess Gibbs free energy (\bar{G}_{Sr}^{E}) was also calculated using Equation 2.12. The resulting values are listed below in Table 2.14 and are depicted graphically for T = 950 K in Figure 2.24a-c.

Ye		$E\left(\mathrm{V}\right)$		$\ln a_{ m Sr}$			$\bar{G}_{\rm Sr}^{\rm E}$ (kJ mol ⁻¹)		
ASr	850 K	950 K	1050 K	850 K	950 K	1050 K	850 K	950 K	1050 K
0.03	0.860	0.874	0.888	-23.5	-21.4	-19.6	-192	-198	-204
0.05	0.849	0.860	0.871	-23.2	-21.0	-19.3	-185	-190	-194
0.08	0.818	0.825	0.832	-22.3	-20.2	-18.4	-176	-180	-183
0.10	0.805	0.811	0.817	-22.0	-19.8	-18.1	-172	-175	-178
0.15	0.775	0.777	0.779	-21.2	-19.0	-17.2	-163	-165	-167
0.20	0.722	0.721	0.719	-19.7	-17.6	-15.9	-151	-152	-153
0.25	0.714	0.687	0.683	-19.5	-16.8	-15.1	-148	-144	-144
0.30	0.704	0.646	0.623	-19.2	-15.8	-13.8	-144	-134	-131
0.35	0.703	0.646	0.592	-19.2	-15.8	-13.1	-143	-133	-123
0.40	0.681	0.639	0.585	-18.6	-15.6	-12.9	-138	-131	-121
0.45	0.684	0.641	0.585	-18.7	-15.7	-12.9	-138	-130	-120
0.50	0.571	0.557	0.543	-15.6	-13.6	-12.0	-115	-113	-111

Table 2.14. Measured emf, natural log of the activity of Sr in Sn, and the measured excess partial molar Gibbs energy of strontium for mole fractions $x_{Sr} = 0.03$ to $x_{Sr} = 0.50$.







Figure 2.24. (a) Measured emf values (E_{cell}), (b) natural log of activity (ln a_{Sr}), and (c) excess molar partial Gibbs energy (\overline{G}_{Sr}^{E}) as a function of x_{Sr} at 950 K.

Figure 2.24a presents the emf values as a function of Sr mole fraction (x_{Sr}) with the liquidus composition and intermetallic phases superimposed at 950 K. The emf clearly decreases as a function of x_{Sr} until reaching the [L = L + SrSn₃] transition, at which point the emf becomes constant with respect to x_{Sr} . As mole fraction increases past the liquidus temperature the emf is observed to remain constant within distinct phase domains, dropping only at the boundaries between two-phase regions; this behavior is coherent with respect to theory as activity is constant within two-phase regions and only changes at the boundaries. Figure 2.24b and Figure 2.24c depict the natural logarithm of activity of Sr in Sn and the partial molar excess Gibbs energy of Sr respectively as functions of x_{Sr} at 950 K. The activity of Sr in Sn in the $x_{Sr} = 0.03$ alloy at 950 K is $a_{Sr} = 5.1 \times 10^{-10}$ with $\bar{G}_{Sr}^{E} = -198$ kJ mol⁻¹ indicating strong atomic interactions, though not as strong as the previously investigated Sr-Bi or Sr-Sb interactions.

2.4.3 Structural Characterization of the Sr-Sn System

Crystal structures of the Sr-Sb alloys were characterized in the same manner as described for the Sr-Bi and Sr-Sb systems, i.e. alloys were annealed under Ar at 15 K below their respective solidus lines (according to Zhao et al. [59]), crushed with a mortar and pestle, and coated with mineral oil to prevent oxidation before being taken to the XRD.

Analysis of the acquired XRD patterns identified the SrSn₄, SrSn₃, Sr₃Sn₅, SrSn, Sr₅Sn₃, and Sr₂Sn phases. The reported crystal structures for the observed phases are available in Table 2.15. All observed crystal structures agree with those found in the phase diagrams proposed by Zhao et al. and Palenzona et al. [58,59]; no new phases were found to exist, nor were any of the currently accepted phases found to be unstable or absent. XRD patterns were determined for the full composition range of the Sr-Sn system instead of only the $0.03 \le x_{Sr} \le 0.50$ composition range investigated via emf measurements to provide the most complete understanding of the phase behavior possible (Figure 2.25a-b). The presence of meta-stable phases was again observed, with the SrSn phase still present at $x_{Sr} = 0.65$ even though the expected phase behavior indicates the Sr₅Sn₃ and Sr₂Sn phases as the only two that should be present. Similarly, the SrSn₄ phase can be seen at $x_{Sr} = 0.40$ as well, despite the expectation of only the Sr₃Sn₅ and SrSn phases. The presence of these non-equilibrium phases is likely due to the short annealing time (24 h)

coupled with the sluggish kinetics of solid-solid phase transitions. Observed phases are listed in Table 2.16 with respect to mole fraction.

Phase	x _{Sr}	Space group	Density	Volume	Lattice paran	neters
		(Pearson symbol)	(mg m ⁻³)	(nm ³)	(nm)	(°)
Sn	0.00	tI4	7.29	0.1081	a=0.58308	α=90
		I41/amd			b=0.58308	β=90
					c=0.3181	γ=90
SrSn ₄	0.20	oS20	6.6	0.5664	a=0.46179	α=90
		Cmcm			b=1.7372	β=90
					c=0.706	γ=90
SrSn ₃	0.25	hR48	6.42	1.3769	a=0.694	α=90
		<i>R-3m</i>			b=0.694	β=90
					c=3.301	γ=120
Sr ₃ Sn ₅	0.38	oS32	5.75	0.9889	a=1.061	α=90
		Cmcm			b=0.8557	β=90
					c=1.0892	γ=90
SrSn	0.50	oS8	5.02	0.27297	a=0.5045	α=90
		Cmcm			b=1.204	β=90
					c=0.4494	γ=90
Sr ₅ Sn ₃	0.63	tI32	4.5	1.17128	a=0.854	α=90
		I4/mcm			b=0.854	β=90
					c=1.606	γ=120
Sr ₂ Sn	0.67	oP12	4.29	0.45538	a=0.8402	α=90
		Pnma			b=0.5378	β=90
					c=1.0078	γ=90
Sr (rt)	1.00	cF4	2.58	0.2253	a=0.60849	α=90
		Fm-3m			b=0.60849	β=90
					c=0.60849	γ=90

Table 2.15. Reported crystal structures in Sr-Sn system [30,54,56,57,62–65].

Sr (ht)	1.00	cI2	2.55	0.1141	a=0.485	α=90
		Im-3m			b=0.485	β=90
					c=0.485	γ=90





Figure 2.25. X-ray diffraction patterns for selected Sr-Sb alloy compositions (a) $x_{Sr} = 0.05$ to $x_{Sr} = 0.30$ and (b) $x_{Sr} = 0.40$ to $x_{Sr} = 0.65$ with standard reference patterns denoted (*) [23,38].

Table 2.16. Crystal structures identified by XRD pattern analysis at each mole fraction for the Sr-Sn system.

Mole Fraction, x_{Sr}	Phases Observed
0.05, 0.15	Sn, SrSn4
0.20, 0.25, 0.30	Sn, SrSn ₄ , SrSn ₃
0.40	Sn, SrSb ₃ , Sr ₃ Sn ₅
0.55	Sr ₃ Sn ₅ , SrSn
0.60, 0.65	SrSn, Sr ₅ Sn ₃
0.75	SrSn, Sr ₅ Sn ₃ , Sr

2.4.4 Thermal Analysis and Phase Transitions

DSC analysis was performed in the same manner as for the Sr-Bi and Sr-Sb systems. For solidus lines, the onset temperatures from each scan rate were averaged to calculate the transitions temperature and for liquidus lines, the peaks from each scan rate were extrapolated to a scan rate of 0 K min⁻¹ [66]. The Sr-Sn alloys with $x_{Sr} > 0.35$ began to react with the alumina crucible, and therefore no DSC measurements were performed above compositions of $x_{Sr} = 0.35$.

The 20 K min⁻¹ scan is depicted for each composition (Figure 2.26) over a temperature range T = 400-1050 K. Several major transitions were observed over the composition range: the liquidus temperature for several of the tested compositions (*); the transition [L + SrSn₄ = SrSn₄ + Sn] at ~501 K (I); the transition [L + SrSn₃ = SrSn₄] at ~623 K (II); and the transition [L + Sr₃Sn₅ = +SrSn₃] at ~868 K (III). For the liquidus measurements, DSC transition temperatures agreed with the emf transition temperatures within 12 K and DSC measurements for the solidus transition were self-consistent within 5 K over all measured compositions and consistent with the emf transition temperatures within 12 K. The visibility of the transition at 623 K in the $x_{Sr} = 0.25$ sample confirms the meta-stability noted during the emf and XRD measurements.



Figure 2.26. Differential scanning calorimetry data for Sr-Sn compositions $0.03 \le x_{Sr} \le 0.35$ collected at a scan rate of 20 K min⁻¹.

A comparison of transitions predicted by emf and DSC is provided in Table 2.17 below.

X _{Sr}		T _{liquidus} (K)		
	emf/DSC	emf/DSC	emf/DSC	emf/DSC
	Ι	II	III	*
0.03	—/504	/	/	/
0.05	—/503	/	/	/
0.08	—/501	—/625	/	/
0.10	—/501	—/626	/	/
0.15	—/500	—/623	/	738/735
0.20	—/500	—/624	/	831/832
0.25	/	—622	/	878/866
0.30	/	/	880/868	987/989
0.35	/	/	879/868	1049/1059
0.40	/	/	/	1076/—
0.45	/	/	/	1106/—

Table 2.17. Summary of liquidus and other transitions as determined by emf and DSC measurements for the Sr-Sn system.

2.4.5 Verification of the Sr-Sn Phase Diagram

The phase transition data from the emf and DSC measurements (Table 2.17) was overlaid onto the Sr-Sn phase diagram created by Zhao et al. [59] to assess the accuracy of the experimental work as well as the reliability of the computational model. The Sr-Sn phase diagram from Zhao et al. was reproduced with the CALPHAD technique using the thermodynamic parameters listed in the paper, the result is depicted below in Figure 2.27.



Figure 2.27. Sr-Sn phase diagram reproduced from Zhao et al. [59] using CALPHAD modeling compared with the experimental data from this work.

The calculated phase transitions from emf and DSC show reasonable agreement with the computationally developed phase diagram; however, the transitions predicted by the model at 586 K and 834 K are ~40 K below the measured transitions. While the exact reason for this deviation is unknown, it is worth noting that other experimental works including Widera and Schafer [54] as well as Ray [53] indicate a similar deviation (~40 K above the modeled transition). Due to the excellent agreement between the DSC and emf data, the phase transition temperatures predicted

in this work may make a valuable addition to the computational model of the Sr-Sn system. All phases indicated in the phase diagram were confirmed via XRD measurements; therefore, unlike the Sr-Bi and Sr-Sb systems, no changes regarding the choice of existent phases are recommended.

2.4.6 Summary of the Sr-Sn System

This study has determined thermodynamic properties of the binary Sr-Sn system, including activities, partial molar entropies, enthalpies, and excess Gibbs energies; X-ray diffraction measurements also confirmed the current phase description of the system. The strong atomic interactions between Sr and Sb (a_{Sr} as low as 7.6×10^{-10} at 950 K and $x_{Sr} = 0.05$) indicate promise as an electrode material for separating dissolved strontium ions (Sr²⁺) from molten salt electrolytes (e.g., LiCl-KCl-SrCl₂), though less so than the Sr-Sb and Sr-Bi systems as the activity of Sr in Sn is approximately 2 orders of magnitude higher.

2.5 Summary on the Sr-Bi, Sr-Sb, and Sr-Sn Systems

The Sr-Bi, Sr-Sb, and Sr-Sn binary alloy systems were investigated via the electromotive force technique, X-ray diffraction, and differential scanning calorimetry in order to elucidate fundamental thermochemical data and phase behavior. The emf measurements provided thermodynamic properties including activity, partial molar entropy, and partial molar enthalpy; these data allow for prediction of the shifts in standard reduction potential indicated by the Nernst equation and analysis of the viability of each liquid metal for removing Sr^{2+} from molten salts. The XRD patterns either succeeded in confirming the known phase behavior of the systems (Sr-Sn) or helped to develop new phase understanding (Sr-Bi and Sr-Sb) resulting in significant changes to existing phase diagrams. DSC measurements provided a secondary method of determining phase transition temperatures to compare with the emf results; these data allowed for the development of new phase diagrams as well as further confirmation of the accuracy of the emf measurements.

In the process of evaluating Bi, Sb, and Sn as liquid metal electrodes for purification of contaminated electrorefiner molten salt electrolytes, a wealth of thermodynamic data was acquired and understanding of the phase behavior for several binary alloy systems was significantly improved.

Chapter 3. Electrochemical Deposition into Liquid Metal Electrodes

3.1 Shift in Redox Potentials in Liquid Metals

By using the activity values determined for Sr(in Bi) as well as known activity values for Li(in Bi) and K(in Bi) [67,68], the shift in standard reduction potentials of Sr²⁺, Li⁺, and K⁺ due to their strong atomic interactions with Bi can be predicted using the Nernst equation (Equation 2.11). An altered deposition sequence is predicted, showing the initial redox potentials of the alkali/alkaline-earth metals [69] as well as the shifts determined for $x_{A(in Bi)} = 0.05$ and $x_{A (in Bi)} = 0.10$ using the activities determined via emf measurements in Chapter 2.2 (Figure 3.1).



Figure 3.1. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(\text{in Bi})} = 0.05$ to $x_{A(\text{in Bi})} = 0.10$ compared to the standard electrode potentials (circle) at 500 °C [69]. Each arrow represents the shift in potential due to the activity of A in the Bi electrode.

As is clearly indicated in Figure 3.1, the redox potential of Sr^{2+}/Sr experiences the largest shift due to the Bi electrode, resulting in an altered deposition sequence. With an inert electrode, the deposition order is given by: $Li \rightarrow Sr \rightarrow K$; however, with the strongly interacting Bi electrode, an altered deposition order is predicted: $Sr \rightarrow Li \rightarrow K$. While there is a degree of overlap between the Sr and Li redox potentials dependent on the amount of Li or Sr in the Bi electrode, it remains clear that the deposition sequence has changed to the benefit of removing more Sr from the salt.

Similarly, the activity data from the Sr-Sb emf measurements can be used to predict the effect of using an Sb electrode (Figure 3.2) [67,70,71].



Figure 3.2. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(in Sb)} = 0.05$ to $x_{A(in Sb)} = 0.10$ compared to the standard electrode potentials (circle) at 650 °C [69]. Each arrow represents the shift in potential due to the activity of A in the Sb electrode.

The Sb liquid metal electrode predicts a substantial shift in the Sr²⁺/Sr redox potential, larger than the shift indicated with the Bi electrode (+1.00 V for Bi vs. +1.15 V for Sb); however, the shift in the Li⁺/Li redox potential is larger due to the Sb electrode as well, resulting in the same predicted redox potentials for both (-2.47 V at both $x_{Sr} = 0.05$, $x_{Li} = 0.05$). While the shift remains beneficial due to the proportionally larger amount the Sr²⁺/Sr redox potential moves, co-deposition of Sr and Li is likely as they have the same predicted redox potential into Sb at $x_A = 0.05$. The shift in redox potentials were calculated in the same manner for a Sn electrode using the activity values determined in Chapter 2.4 for Sr(in Sn) [72–74] (Figure 3.3).



Figure 3.3. Equilibrium potentials of the Sr, Li, and K redox couples at $x_{A(in Sn)} = 0.05$ to $x_{A(in Sn)} = 0.10$ compared to the standard electrode potentials (circle) at 500 °C [69]. Each arrow represents the shift in potential due to the activity of A in the Sn electrode.

As indicated by Figure 3.3, the shift in the Sr^{2+}/Sr redox potential is low compared to Sb or Bi (0.80 V), and while the shift in the Li⁺/Li redox potential is also lower, the predicted shift due to Sn places the Sr^{2+}/Sr couple at -2.82 V at $x_{Sr} = 0.05$ whereas the Li⁺/Li couple is more negative at -2.84 V at $x_{Li} = 0.05$. This implies that the Sn electrode will likely not be able to achieve a favorable ratio of Sr to Li deposition.

3.2 Electrochemical Deposition Cell Design

Based on the activity values of Sr (in Bi, Sb, and Sn) measured using the electromotive force measurements in Chapter 2, Sb and Bi are predicted to be able to separate Sr most preferentially from molten chloride electrolytes, with Sn showing the least promise due to weaker atomic interactions with Sr^{2+} . In order to confirm the theory provided by the emf measurements, an electrochemical cell was developed to examine the ability of each liquid metal electrode to preferentially remove Sr from LiCl-KCl-SrCl₂. A three-electrode cell was utilized, with the liquid metal of interest (i.e. Bi, Sb, Sn) acting as the working electrode, an inert graphite rod acting as the counter electrode, and a Ag^+/Ag reference electrode [75].

3.2.1 Electrolyte Preparation

LiCl-KCl-SrCl₂ (56.7-38.3-5 mol%) electrolyte was prepared from appropriate weights of LiCl (Ultra dry, 99.9%, Alfa Aesar, Product No. 14540), KCl (Ultra dry, 99.95%, Alfa Aesar, Product No. 14466), and SrCl₂ (anhydrous, 99.5%, Alfa Aesar, Product No. 16790). The electrolyte was then loaded into a quartz crucible (Technical Glass Products) for pre-melting in a stainless steel vacuum chamber. The chamber was loaded in a crucible furnace (Mellen, CC-12), evacuated to less than 10 mtorr, and heated under vacuum at 100 °C for 12 h and at 270 °C for 12 h to remove residual moisture and oxygen. The chamber was then purged with ultra-high purity argon three times and heated to 700 °C for 3 h under a slowly flowing (50 mL min⁻¹) argon atmosphere. After cooling, the dry and homogeneous electrolyte was ground into a fine powder using a mortar and pestle for use in the electrochemical cell.

3.2.2 Electrode Preparation

Bi working electrodes were prepared from bismuth pieces by melting 3.50 g of Bi inside a boron nitride (BN) crucible (Saint-Gobain Advanced Ceramics, Product No. AX05), using an induction heater (IH15A-2T, Across International) custom-installed inside a glove box (< 0.5 ppm O_2). The dimensions of the BN crucible were 20 mm in height, 12 mm outer diameter, 8 mm inner diameter, and 15 mm in depth, giving a nominal surface area of 0.5 cm². A tungsten wire was inserted into the liquid Bi to establish electrical contact during induction heating. A graphite rod (0.95 cm in diameter and 5 cm in length) was used as the counter electrode (CE), female-threaded at the top and connected to a male-threaded steel rod for electrical connection. The Ag/Ag⁺ reference electrode (RE) was constructed using a closed-end mullite tube (6.4 mm in outer diameter and 45.7 cm in length) which contained ~0.5 g of LiCI-KCI-AgCl electrolyte and Ag wire (1 mm in diameter and 48.3 cm in length, 99.9%, Alfa Aesar, Product No. 11434) to establish a reversible half-cell potential. The reference electrolyte was prepared using the same procedures as described earlier by adding 1 wt% of AgCl (anhydrous, 99.998%, Sigma Aldrich, Product no. 449571) into eutectic LiCI-KCI.

3.2.3 Cell Preparation and Assembly

The electrodes and thermocouple (ASTM Type K) were arranged inside an alumina crucible (60 mm in diameter and 100 mm in height; Advalue Technology, Product No. AL-2250) and then, ~100 g of the electrolyte was added over the electrodes. The assembled cell was placed into a test chamber; the chamber was sealed inside the glovebox and loaded into a crucible furnace. The chamber was first evacuated and dried, following a similar procedure for preparing the electrolytes, and then was purged with ultra-high purity argon gas three times and heated to 500
°C under a slowly flowing (50 mL min⁻¹) argon atmosphere. The electrodes were allowed to equilibrate for 12 h at 500 °C for electrochemical measurements. The cell temperature was monitored and recorded using a data acquisition board (National Instruments, NI 9211).

3.3 Electrochemical Deposition of Sr into Bi

The electrochemical deposition into liquid Bi was implemented using the graphite CE and the Ag/Ag⁺ RE at 500 °C, in LiCl-KCl-SrCl₂. The Bi WEs were cathodically discharged to the specific charge capacity (coulombs per gram of Bi) of 270 C g⁻¹ under constant current control ($j = -50 \text{ mA cm}^{-2}$) using a potentiostat-galvanostat (Autolab PGSTAT302N). After deposition experiments, the cell was cooled to room temperature and the discharged Bi electrodes were isolated from the cell assembly. The Bi electrodes were rinsed with deionized water to remove entrained salt from the surface, and cross-sectioned for compositional and microstructural analyses. The electrodes were mounted in epoxy, polished using silicon carbide emery paper (up to 1200 grit) with mineral oil as a lubricant to minimize reaction with moisture and oxygen, and characterized using SEM-EDS (Figure 3.4).



Figure 3.4. SEM/EDS images of the Bi electrode following deposition to a specific capacity of 270 C g⁻¹ at 500 °C in LiCl-KCl-SrCl₂ (56.7-38.3-5 mol%).

The microstructural features of the Bi electrode, elucidated by SEM-EDS, included Bi as well as the intermetallic phase of Sr-Bi (29-71 mol%), which agrees well with the expected phase behavior for the Sr-Bi system: Bi + SrBi₃. The unidentified region lacking both Sr and Bi (i.e., dark region in Figure 3.4), suggests the presence of Li, which cannot be detected by EDS due to its low atomic weight.

The compositions of the electrodes were also determined using inductively coupled plasma-atomic emission spectroscopy with a precision of 4% of the measured value (Table 3.1).

Table 3.1. The composition of Bi electrodes after deposition to the specific capacity of 270 C g⁻¹ at 500 °C in eutectic LiCl-KCl electrolyte containing 5 mol% of SrCl₂ by ICP-AES and the estimated coulombic efficiency.

Compo	sition of l	Coulombic		
Li	Κ	Sr	Bi	efficiency (%)
16.2	0.7	6.5	76.6	67%

In addition to confirming the deposition of Sr by EDS, the presence of Li in the Bi electrode was evident with 16.2 mol% of Li in Bi and minimal presence of K, confirming that the dominant cathodic reactions were the co-deposition of Sr and Li. The overall coulombic efficiency of the discharge process was estimated to be 67% by comparing the charge required for the measured electrode composition to the total charge passed during electrolysis (270 C g^{-1}). The loss in coulombic efficiency is thought to come from the high reactivity of alkali/alkaline-earth metals which could result in their selective loss during sample preparation using deionized water to eliminate entrained salts for ICP-AES, and back dissolution of alkali/alkaline-earth elements into the electrolyte during electrolysis up to 270 C g^{-1} at 500 °C. The successful deposition of Sr into the Bi electrode confirms the theory posited by the thermodynamic properties; although, the co-deposition of Li indicates that the standard reduction potentials overlap enough that significant amounts of Li will still be removed from the electrolyte.

3.4 Electrochemical Deposition of Sr into Sb, Sn

The same deposition procedure as described above for the Bi electrode was applied to Sb (at 650 °C instead of 500 °C due to the higher melting temperature of Sb: $T_m = 631$ °C) and Sn electrodes by Nigl et al. [76] in order to investigate their potential for electrochemical separations.

The compositions of the electrodes were determined using inductively coupled plasmaatomic emission spectroscopy with a precision of 4% of the measured value (Table 3.2).

Table 3.2. The composition of liquid metal electrodes after deposition to the specific capacity of 200 C g⁻¹ at the specified cell temperatures in eutectic LiCl-KCl electrolyte containing 5 mol% SrCl₂ by ICP-AES [76].

Liquid metal electrode (M)	Composition of liquid metal electrode (mol%)					
	Li	K	Sr		М	
Sn	8.65	0.00	0.00		91.35	
Sb	8.21	1.39	4.07		86.33	

The ICP-AES data concurs with the SEM-EDS results, indicating co-deposition of Sr and Li into the Sb electrode and the potential strength of the Sb electrode as an option for removing Sr from molten salt electrolytes; negligible Sr deposition was observed into the Sn electrode, confirming that Sn does not have strong enough atomic interactions to be of significant use for separating Sr from molten salt electrolytes on its own.

3.5 Summary: Deposition into Liquid Bi, Sb, and Sn Metals

The measurements performed on the liquid metal electrodes to test their relative ability to remove Sr from LiCl-KCl-SrCl₂ electrolyte confirmed what the electromotive force measurements

predicted; the stronger atomic interactions between Sr and Sb as well as Sr and Bi are enough to deposit significant amounts of Sr (4.1 mol% and 6.5 mol%, respectively). Although direct comparison is difficult due to the differences in amount of charge passed depth of deposition, it is clear that both metals have behaved as predicted by the thermodynamic analysis. Sn, on the other hand, seems to be unable to remove an appreciable amount of Sr from the electrolyte (0.0 mol%), which makes sense considering the activity of Sr (in Sn) is ~2-3 orders of magnitude higher than for Sr (in Bi) or Sr (in Sb). Based on these results, pursuing Bi and Sb liquid metal electrodes for removing Sr²⁺ from contaminated electrorefiner salts is a preferable option to Sn; although, Sn could possibly be used in an alloy liquid metal electrode, e.g. Bi-Sn or Sb-Sn as a method of reducing the cost or lowering the melting temperature while retaining the separation abilities. Overall, the results of this work suggest that the electrochemical separation and recovery of Sr fission products into liquid electrodes from molten salt electrolyte is feasible for recycling the process salt (LiCl-KCl) in order to minimize the generation of additional nuclear wastes.

Chapter 4. Thermodynamic Modeling Using First-**Principles Calculations and the CALPHAD Technique**

4.1 Computational Efforts on the Sr-Sb System

Computational approaches to investigating and refining phase diagrams have already been mentioned in this work with Wang et al.'s [16] revisions to the Sr-Bi phase diagram and Zhao et al.'s [59] refinement of the Sr-Sn phase diagram. These studies employed a hybrid approach, using first-principles calculations based on density functional theory (DFT) to assess the stability of viable intermetallic compounds and then incorporating these calculations into the CALculation of Phase Diagrams (CALPHAD) technique using the ThermoCalc software. In both cases, the combination of experimental data with a computational approach resulted in a more accurate phase description for the system, confirmed by the excellent agreement between the high-quality experimental results generated in this dissertation and the computational assessments of the Sr-Bi and Sr-Sn systems.

4.1.1 Necessity of Computational Corroboration for the Sr-Sb System

The lack of a computational description for the Sr-Sb system as well the drastic changes proposed, i.e. the removal of the SrSb₃, SrSb, and Sr₃Sb₂ phases and the addition of the SrSb₂, Sr₂Sb₃, Sr₁₁Sb₁₀, Sr₁₆Sb₁₁, and Sr₅Sb₃ phases, necessitate further investigation of the system to confirm the predicted changes. As such, a computational approach using a combination of first-principles calculations and the CALPHAD technique was applied to the Sr-Sb system in order to complete understanding of the Sr-Sb phase behavior [40]. The phase behavior of the Sr-Sb system predicted using X-ray diffraction (XRD) was corroborated with first-principles DFT-based

calculations, which were used to confirm the stability of all phases noted by XRD (SrSb₂, Sr₂Sb₃, Sr₁₁Sb₁₀, Sr₁₆Sb₁₁, and Sr₅Sb₃) as well as to confirm the instability of several phases suggested in previously published phase diagrams (SrSb, SrSb₃, and Sr₃Sb₂). The DFT calculations were then combined with the activity data from the emf measurements as well as phase transition data from differential scanning calorimetry (DSC) measurements using the CALPHAD technique to develop the revised Sr-Sb phase diagram depicted in Figure 2.21.

4.1.2 First-principles Calculations

To corroborate the experimental XRD results, first-principles calculations were performed to determine the theoretical stability of all the phases present in the Sr-Sb system, both those predicted via the aforementioned XRD as well as those predicted in previous phase diagrams which the XRD determined not to be present. DFT-based first-principles calculations were completed on eight intermetallic compounds i.e. system: SrSb₂, Sr₂Sb₃, Sr₁₁Sb₁₀, Sr₂Sb, Sr₃Sb₂, Sr₁₆Sb₁₁, and two crystal structures (hex and ortho) for the Sr₅Sb₃ intermetallic. The Vienna Abinitio Simulation Package (VASP) was used to perform the first-principles calculations [77]. The lowest energy structures were obtained from the Materials Project for all the intermetallics [38,46,47,49,50,78–82], except Sr₁₆Sb₁₁ [33]. The relaxed structures were deformed into 5 different volumes in order to complete an equation of state (EOS) fitting of the energy vs. volume (*E-V*) curve. A four-parameter Birch-Murnaghan EOS equation was used based on the suggestion by Shang et al. [83]:

$$E_0(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}$$
(4.1)

, where a, b, c and d are fitting parameters. From the EOS fitting, the equilibrium properties at 0 K without the contribution of zero-point vibration energy, including equilibrium volume (V), energy (E), bulk modulus (B), and the first derivative of bulk modulus with respect to pressure (B') were calculated. The finite temperature properties were approximated with the Neumann-Kopp approach. The projector augmented-wave (PAW) method [84,85] was used to describe the electron-ion interactions with the exchange correlation functional elucidated by the generalized gradient approximation (GGA) implemented by Perdew and Wang (PW91) [86]. A sigma value of 0.2 eV and a plane wave energy cutoff of 1.3 times higher than the highest default cutoff were adopted. The Brillouin zone sampling was done with Blöchl corrections [85] using a gamma centered Monkhorst-Pack (MP) scheme [87]. The k-points grid used was an automated k-point mesh generator in VASP with the length of the subdivisions specified as 50 Å. The energy convergence criterion of the electronic self-consistency was set as 10⁻⁴ eV atom⁻¹ with a stopping criteria for the ionic relaxation loop of 10⁻⁴ eV A⁻¹ for all of the calculations. In order to ensure the accuracy of the DFT-based first-principles calculations, the lattice parameters and equilibrium properties including volume (V), energy (E), bulk modulus (B), and first derivative of bulk modulus with respect to pressure (B') were compared with both previous experimental and DFTcalculated results. The lattice parameters from the DFT-based first-principles calculations vary from the experimentally determined lattice parameters by less than 0.07 nm; this variance is quite small and can be attributed to the temperature difference between the calculations (0 K) and experiments (> 130 K). With the accuracy of the calculations verified, the enthalpy of formation of the intermetallic compounds is calculated at 0 K and plotted in Figure 4.1.



Figure 4.1. The formation energy of the intermetallics as a function of temperature from DFTbased first-principles calculations, where \Box represent the enthalpies of formation computed via DFT and the line (convex hull) was determined using CALPHAD modeling.

The first-principles results indicate the stability of $Sr_{16}Sb_{11}$ and $Sr_{11}Sb_{10}$ as well as the Sr_2Sb , $SrSb_2$, and Sr_2Sb_3 phases as evidenced by their close proximity to the convex hull. Also, Sr_5Sb_3 in the hexagonal structure is found to be more stable than the orthorhombic structure and Sr_3Sb_2 is found to be a metastable structure at all temperatures. Based on the excellent agreement between the first-principles analysis and the XRD measurements for the stability of $SrSb_2$, Sr_2Sb_3 ,

Sr₁₁Sb₁₀, Sr₁₆Sb₁₁, Sr₅Sb₃ (hex), and Sr₂Sb phases, confidence in the experimentally determined results is increased.

4.1.3 The CALPHAD Technique

The results of the first-principles calculations were used to assist in the thermodynamic CALPHAD modeling; the ThermoCalc software [40] was used to describe the Gibbs energy equations by the Redlich-Kister polynomial equations [88] described by:

$$G_m^{\phi} = x_A G_A^{\phi} + x_B G_B^{\phi} + RT(x_A \ln x_A + x_B \ln x_B) + {}^E G_m^{\phi}$$
(4.2)

, where x_A and x_B are mole fractions of pure elements A and B, respectively, and G_A^{ϕ} and G_B^{ϕ} are the pure element Gibbs energy functions taken from the SGTE database compiled by Dinsdale [89]. The second part of the equation describes the ideal interactions between the elements, where *R* is the ideal gas constant and *T* is the temperature. Finally, the excess Gibbs energy (${}^EG_m^{\phi}$) describes the non-ideal interactions between elements and is expressed [88]:

$${}^{E}G_{m}^{\phi} = x_{A}x_{B}\sum_{j}{}^{j}L^{\phi}(x_{A} - x_{B})^{j}$$
(4.3)

, where ${}^{j}L^{\phi}$ is the interaction parameter described by:

$$L^{\phi} = a + bT \tag{4.4}$$

, where *a* and *b* are modeled interaction parameters representing the enthalpy and entropy, respectively. Previous modeling of binary systems has shown that in most cases only two interaction parameters are needed to describe the non-ideal interaction between solution phases. The intermetallic compounds were treated as stoichiometric compounds (A_qB_p) and modeled by:

$$G_m^{A_q B_p} = q GHSER_A + p GHSER_B + a + bT$$
(4.5)

, where a and b are fitting parameters representing the enthalpy and entropy, respectively, p and q represent the number of A and B in the stoichiometric compound and $GHSER_A$ and $GHSER_B$ represent the Gibbs energy functions of element A and B in their standard element reference state (SER) at ambient temperature and pressure (Sr is fcc and Sb is rhombohedral).

In order to describe the activity measurements observed in the liquid, the associate solution model is applied in the database. The associate species chosen in this model was Sr_3Sb_2 due to its high melting temperature, i.e. proximity to liquid phases; though $Sr_{16}Sb_{11}$ is the stable phase with the highest melting temperature, it was avoided as a result of the complexity of its crystal structure and size which would have slowed calculations down considerably. Sr_3Sb_2 is one of the closest phases to $Sr_{16}Sb_{11}$ and also represents the natural valence of the constituents, i.e. +2 for Sr and -3 for Sb, making it a reasonable substitute. The Gibbs energy of the associate species is described as,

$${}^{0}G_{Sr_{3}Sb_{2}}^{Liq} = \frac{3}{5} {}^{0}G_{Sr}^{Liq} + \frac{2}{5} {}^{0}G_{Sb}^{Liq} + A + BT + CTlnT$$
(4.6)

, where A, BT and CTInT are the model parameters for the Gibbs energy of formation of the associate species relative to the pure Sr and Sb liquid phases. The results were used to assist in the thermodynamic CALPHAD modeling.

The developed CALPHAD model was used to predict the activity values of x_{Sr} at 988 K and was compared to the experimental results from the electromotive force measurements (Figure 4.2).



Figure 4.2. Comparison of modeled activity of Sr in Sb vs. the activity values determined from the electromotive force measurements at 988 K.

Figure 4.2 presents the natural logarithm of activity values as a function of Sr mole fraction (x_{Sr}) at 988 K comparing the experimentally determined emf values with the activity predicted using the CALPHAD technique. The activity decreases as a function of x_{Sr} until hitting the liquidus composition, at which point it becomes essentially constant with respect to x_{Sr} in the two-phase regions; this invariance is a result of the chemical potential of Sr being constant in two-phase regions. The experimental values agree superbly with the CALPHAD-based model in the liquid phase, but begin to deviate from the theory further with when entering solid-solid phase regions.

This phenomenon is likely due to the presence of non-equilibrium phases at higher x_{Sr} compositions indicated by the XRD measurements; for instance, trapped meta-stable Sr_5Sb_3 (hex) at $x_{Sr} = 0.69$ would result in a higher experimentally determined emf, i.e. lower activity, when compared to the theoretical model which assumes an $x_{Sr} = 0.69$ alloy to contain Sr_2Sb and Sr only.

Based on the emf and DSC data, as well as the first principles calculations, CALPHAD modeling was performed to develop the Sr-Sb phase diagram (Figure 4.3); model parameters are listed in Table 4.1.



Figure 4.3. Computationally constructed Sr-Sb phase diagram using the CALPHAD technique, based on experimental data from emf/DSC measurements, first-principles calculations, as well as thermal analysis from Vakhobov et al. [41].

Phase (model)	Modeled Parameters				
fcc (Sr, Sb)	${}^{0}L_{\rm Sr,Sb}^{\rm fcc} = -19.888 + 1.052 * T$				
Rhombohedral (Sr, Sb)	$^{0}L_{\rm Sr,Sb}^{\rm rhom} = -25,926.413 + 0.995 * T$				
Liquid (Sr, Sb)	$G_{\text{Sr3Sb2}}^{\text{liquid}} = 2 * G_{\text{Sb}}^{\text{Liq}} + 3 * G_{\text{Sr}}^{\text{Liq}} - 480,500 + 1.05 * T$				
	${}^{0}L_{\mathrm{Sr,Sr_3Sb_2}}^{\mathrm{liquid}} = -15,006$				
	${}^{0}L^{\text{liquid}}_{\text{Sr}_{3}\text{Sb}_{2},\text{Sb}} = -110,110$				
	${}^{1}L_{\mathrm{Sr}_{3}\mathrm{Sb}_{2},\mathrm{Sb}}^{\mathrm{liquid}} = -35,000.8$				
$SrSb_2$	$G^{\text{SrSb}_2} = {}^{0}G^{\text{fcc}}_{\text{Sr}} + 2 * {}^{0}G^{\text{rhom}}_{\text{Sb}} - 199,922 - 7.7 * T$				
Sr ₂ Sb ₃	$G^{\text{Sr}_2\text{Sb}_3} = 2 * {}^0G^{\text{fcc}}_{\text{Sr}} + 3 * {}^0G^{\text{rhom}}_{\text{Sb}} - 397,906.48 - 13 * T$				
$\mathbf{Sr}_{11}\mathbf{Sb}_{10}$	$G^{\text{Sr}_{11}\text{Sb}_{10}} = 11 * {}^{0}G^{\text{fcc}}_{\text{Sr}} + 10 * {}^{0}G^{\text{rhom}}_{\text{Sb}} - 2,045,599$				
$Sr_{16}Sb_{11}$	$G^{\text{Sr}_{16}\text{Sb}_{11}} = 16 * {}^{0}G^{\text{fcc}}_{\text{Sr}} + 11 * {}^{0}G^{\text{rhom}}_{\text{Sb}} - 2,785,080 + 66 * T$				
Sr ₅ Sb ₃	$G^{\text{Sr}_5\text{Sb}_3} = 5 * {}^0G^{\text{fcc}}_{\text{Sr}} + 3 * {}^0G^{\text{rhom}}_{\text{Sb}} - 791,786 + 20.5 * T$				
Sr ₂ Sb	$G^{\text{Sr}_2\text{Sb}} = 2 * {}^{0}G^{\text{fcc}}_{\text{Sr}} + {}^{0}G^{\text{rhom}}_{\text{Sb}} - 265,438 + 6.9 * T$				

Table 4.1. Modeled parameters in SI units for the phases in the Sr-Sb binary system. These

 parameters were incorporated with the SGTE data for the pure elements.

The strength of the correlation between the experimentally determined XRD and emf data with the computational first-principles and CALPHAD analysis was useful in developing the Sr-Sb system and providing the most complete thermodynamic understanding possible. As such, refining previously analyzed systems using computational method in conjunction with the activity values and transitions determined using emf data will certainly be an aspect of future research in this field.

Chapter 5. Conclusions and Future Work

5.1 Summary and Conclusions

The presence of radioactive fission products such as ¹³⁷Cs and ⁹⁰Sr which oxidize from used nuclear fuels during the electrorefining process necessitates frequent disposal and replacement of the electrolyte, thereby increasing the amount of nuclear waste accumulating in onsite storage facilities without long-term contingency plans for disposal. The primary objective of this dissertation was to determine the viability of liquid metal electrodes for separating Sr^{2+} from molten salt electrolytes with the intention of providing a route towards removing Sr from contaminated electrorefiner LiCl-KCl-UCl₃ electrolyte. While an inert cathode will be unable to reduce Sr^{2+} out of the electrolyte without first removing Li due to the order of the standard reduction potentials of the alkali/alkaline-earth elements in the chloride system, liquid metal electrodes (e.g. Bi, Sb, Sn) were postulated to be able to shift the standard reduction potential of Sr^{2+} , possibly allowing preferential deposition of Sr^{2+} out of LiCl-KCl-based molten salts. In order to determine the effectiveness of Bi, Sb, and Sn at potentially altering the redox potential of Sr^{2+}/Sr , electromotive force measurements were conducted for the Sr-Bi, Sr-Sb, and Sr-Sn binary systems to determine the strength of the atomic interactions between Sr and each of the liquid metals, i.e. the activity of Sr (in liquid metal, B). The electromotive force measurements concluded that Sr-Sb exhibits the strongest interactions with Sr (a_{Sr} as low as 1.5×10^{-12} at 988 K and $x_{Sr} = 0.04$), followed by Sr-Bi (a_{Sr} as low as 2.5×10^{-11} at 988 K and $x_{Sr} = 0.05$), and finally that Sr-Sn exhibits the weakest interactions with Sr (a_{Sr} as low as 7.6 × 10⁻¹⁰ at 950 K and x_{Sr} = 0.05). Based on this behavior, Sb and Bi were predicted to be the most efficient liquid metal electrode options for removing Sr from molten chlorides, which was then confirmed with deposition experiments in which constant current was applied between each of the liquid metal options (Bi, Sb, and Sn) and an inert graphite counter electrode in LiCl-KCl-SrCl₂ molten salt. Post-mortem analysis via ICP-AES compositional analysis indicated significant presence of Sr in the Bi (~6.5 mol%) and Sb (~4.1 mol%) electrodes; however, reasonable amounts of Li were also discovered in each of the electrodes (~16.2 mol% in Bi and ~8.65 mol% in Sb). Despite the undesirable presence of Li, the substantial amount of Sr deposited in the liquid metals is encouraging. Overall, the results indicate that the strong interactions between Sr and Bi, Sb can be leveraged to remove Sr from molten salt electrolytes, providing a potential path towards reducing the volume of nuclear waste sitting idle in temporary storage sites.

In the process of investigating the thermodynamic properties of the Sr-Bi, Sr-Sb, and Sr-Sn systems, XRD and DSC measurements were also performed, which aided in developing new phase diagrams and descriptions of phase behavior in the existing understanding of the binary systems. Two additional phases of Sr₂Bi₃ and Sr₄Bi₃ were indicated, which are not considered in the current Sr-Bi equilibrium phase diagram as a result of these measurements; the presence of the SrSb₂, Sr₂Sb₃, Sr₁₁Sb₁₀, Sr₁₆Sb₁₁, and Sr₅Sb₃ (hex) phases were also determined, resulting in significant alterations to the Sr-Sb phase diagram.

5.2 Future Work: Removal of Cs from Molten Salts

As mentioned in the Chapter 1, Sr is not the only dangerous element to contaminate the electrorefiner molten salt; Cs causes similar problems due to the short half-life and high heat density of the ¹³⁸Cs isotope. Therefore, the ongoing efforts and future direction of this dissertation are largely focused on performing similar thermodynamic property and deposition measurements with the intention of determining the activity of Cs in liquid metals and preferentially removing

Cs from LiCl-KCl-based molten salts. Preliminary deposition experiments were attempted to determine the viability of liquid metal electrodes for removing Cs from LiCl-KCl-CsCl (56.7-38.3-5 mol%). The methods utilized were the same as for the Sr deposition experiments detailed in Chapter 3 for Bi, Sb, and Sn. The Bi and Sn depositions were performed at 500 °C, whereas the Sb deposition was performed at 650 °C due to the melting temperature of Sb. The ICP-AES results from the crushed remnants of the post-mortem electrodes are present below in Table 5.1.

Table 5.1. The composition of liquid metal electrodes after deposition to the specific capacity of 100 C g^{-1} at the specified cell temperatures in eutectic LiCl-KCl electrolyte containing 5 mol% CsCl by ICP-AES.

Liquid metal	Composition of liquid metal electrode (mol%)					
electrode (M)						
	Li	K	Cs	М		
Bi	12.37	0.01	4.33	82.68		
Sb	5.78	0.00	3.00	90.88		
Sn	11.56	0.00	1.21	87.22		

The ICP-AES data confirms the deposition of Cs, although the presence of Li in the liquid metal electrodes was quite evident with 12.37 mol% of Li in Bi, 5.78 mol% in Sb, and 11.56 mol% is Sn, positing that the dominant cathodic reactions were the co-deposition of Cs and Li. Overall, the preliminary results indicate that it is possible to remove Cs from molten chloride salts, much as it was proven possible with Sr; however, further tests and corresponding thermodynamic property calculations will be necessary in order to confirm this behavior.

Unfortunately, electromotive force measurements cannot be performed on Cs in the same manner as for Sr; in the case of the electromotive force measurements on the Sr-M systems, pure

Sr was used as a reference electrode for the development of a calibration curve against a lessreactive and lower melting temperature Sr-Bi alloy. However, pure Cs is much more reactive than pure Sr and also has a much lower melting temperature: $T_{m, Sr} = 777$ °C vs. $T_{m, Cs} = 28$ °C [90]. Attempting to raise a pure Cs electrode to the necessary temperature range of 500-850 °C for the calibration of a Cs-Bi alloy reference is simply not possible; the pure Cs electrode will either completely react with the CaF₂-CsF electrolyte or vaporize. In order to circumvent these issues, a different fluoride-based electrolyte system is recommended: LiF-NaF-KF (FLiNaK) + CsF (45.5-10.5-41-3 mol%). Unlike the CaF₂-SrF₂ (97-3 mol%), the FLiNaK-CsF electrolyte is a liquid in the temperature regime of interest ($T_{m, FLiNaK} = 454 \text{ °C } [91]$), but it still has the necessary high ionic conductivity and low electronic conductivity to function as a viable electrolyte. Using pure Cs as a reference electrode is not possible due to its high reactivity and low melting temperature; therefore, a Ni/Ni²⁺ reference electrode is recommended due to its successful use as a reference electrode in fluoride-based salts [92]. Emf measurements on Cs-M systems would allow for the application of the same methods used to evaluate the Sr-M systems and the potential development of a liquid metal electrode system capable of preferentially removing Cs⁺ from molten salts.

References

- Department of Energy, Nuclear Field Data Survey, U.S. Energy Inf. Assoc. (2013) For GC-859.
- M.F. Simpson, Projected Salt Waste Production from a Commercial Pyroprocessing Facility, 945858 (2013). doi:10.1155/2013/945858.
- [3] F. Study, P. Nuclear, P. Plant, E. County, G. River, The Blue Castle Project : A Feasibility Study of the Proposed Nuclear Power Plant in Emery County , Utah along the Green River, (2015).
- [4] International Atomic Energy Agency, Reference Data Series No. 2 2018 Edition Nuclear Power Reactors in the World, (2018) 79. https://wwwpub.iaea.org/MTCD/Publications/PDF/RDS-2-38_web.pdf.
- [5] A. Witze, US Election: Questioning the Candidates, Nature. 455 (2008) 446–449.
- [6] M.F. Simpson, Developments of Spent Nuclear Fuel Pyroprocessing Technology at Idaho National Laboratory, Idaho Falls, ID, 2012. doi:10.2172/1044209.
- [7] HSC Chemistry 5.1, F. Outokumpu Oy, Finland, (2002).
- [8] J. Bruno, R.C. Ewing, Spent nuclear fuel, Elements. (2006). doi:10.2113/gselements.2.6.343.
- [9] S. Nakayama, Y. Morita, K. Nishihara, H. Oigawa, Partitioning-transmutation technology: a potential future nuclear waste management option, in: Nucl. Energy Agency-Information Exch. Meet., 2005: pp. 347–359.
- [10] H. Kim, N. Smith, K. Kumar, T. Lichtenstein, Electrochemical Separation of Barium into Liquid Bismuth by Controlling Deposition Potentials, Electrochim. Acta. (2016).
- [11] H. Okamoto, Sb-Sr (Antimony-Strontium), Bin. Alloy Phase Diagrams, II Ed., T.B.

Massalski. 3 (1990) 3304–3307.

- [12] H. Okamoto, Bi-Sr (Bismuth-Strontium), Bin. Alloy Phase Diagrams, II Ed. (1990).
- [13] N.D. Smith, T. Lichtenstein, J. Gesualdi, K. Kumar, H. Kim, Electrochimica Acta Thermodynamic Properties of Strontium-Bismuth Alloys Determined by Electromotive Force Measurements, Electrochim. Acta. 225 (2017) 584–591. doi:10.1016/j.electacta.2016.12.051.
- [14] H. Ipser, A. Mikula, I. Katayama, Overview: The emf method as a source of experimental thermodynamic data, Calphad Comput. Coupling Phase Diagrams Thermochem. (2010). doi:10.1016/j.calphad.2010.05.001.
- [15] A. Bard, L. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., John Wiley and Sons, Hoboken, 2001.
- [16] Y. Wang, J. Xin, C. Chen, S. Liu, B. Hu, Y. Du, Thermodynamic assessment of the Sr-In and Sr-Bi systems supported by first-principles calculations, Calphad Comput. Coupling Phase Diagrams Thermochem. (2014). doi:10.1016/j.calphad.2013.12.001.
- [17] J. Delcet, R.J. Heus, J.J. Egan, Electronic Conductivity in Solid CaF at High Temperature,
 J. Solid State Chem. J. Appl. Electrochem. This J. J. Chim. Phys. J. Appl. Electrochem. J.
 Solid State Chem. J. Fouletier J. Solid State Chem. 125 (1976) 369–217.
- [18] N.I. Sorokin, B.P. Sobolev, Solid-State Fluoride Electrolyte Review, Crystallogr. Reports.52 (2007) 842–853.
- H. Kim, D.A. Boysen, D.J. Bradwell, B. Chung, K. Jiang, A.A. Tomaszowska, K. Wang,
 W. Wei, D.R. Sadoway, Thermodynamic properties of calcium–bismuth alloys
 determined by emf measurements, Electrochim. Acta. 60 (2011) 154–162.
 doi:10.1016/j.electacta.2011.11.023.

- [20] S. Poizeau, H. Kim, J.M. Newhouse, B.L. Spatocco, D.R. Sadoway, Determination and modeling of the thermodynamic properties of liquid calcium-antimony alloys, Electrochim. Acta. (2012). doi:10.1016/j.electacta.2012.04.139.
- [21] J.M. Newhouse, S. Poizeau, H. Kim, B.L. Spatocco, D.R. Sadoway, Thermodynamic properties of calcium-magnesium alloys determined by emf measurements, Electrochim. Acta. (2013). doi:10.1016/j.electacta.2012.11.063.
- [22] J. Delcet, J.J. Egan, THERMODYNAMICS OF LIQUID Ca-Ag AND Ca-In ALLOYS, J. Less-Common Met. Elsevier Sequoia S.A. 59 (1978) 229–236.
- [23] R.T. Downs, M. Hall-Wallace, The American Mineralogist Crystal Structure Database,(2003) American Mineralogist 88, 247–250.
- [24] S.A. Shukarev, M.P. Morozova, G.V. Kokosh, N, Zh. Oshch. Khim. 26 (1956) 1525– 1531.
- [25] R.J. Pleasance, No Title, J. Inst. Met. 88 (1959).
- [26] D.G. Schweitzer, J.R. Weeks, Liquid metal fuel constitutions. III. Liquidus curves of the bismuth-fission products systems, Trans. Am. Soc. Met. 54 (1961).
- [27] N.N.Zhuravlev, E.M.Smirnova, Investigation of Alloys of the Bi-Ba and Bi-Sr Systems, Inorg.Mater. (1966) 654–656.
- [28] E.B. Klebanov, O.. Tvaradze, A.G. Moroachevskii, No Title, Tsvetn. Met. 5 (1986) 126–127.
- [29] M.E. Straumanis, The precision determination of lattice constants by the powder and rotating crystal methods and applications, J. Appl. Phys. 20 (1949) 726–734.
 doi:10.1063/1.1698520.
- [30] E.A. Sheldon, A.J. King, Structure of the allotropic forms of strontium, Acta Crystallogr.

6 (1953) 100.

- [31] N.N. Zhuravlev, V.P. Melik-Adamyan, Study of the crystal structure of the superconducting compounds SrBi3 and BaBi3, J. Phys. Chem. Solids. 31 (1970) 2653– 2662.
- [32] F. Mefio, M.L. Fornasini, Crystal Structure of some phases and alloying behavior in alkaline earths, europium, and ytterbium pnictides, Mater. Res. Bull. 29 (1994) 149–154.
- [33] E.A. Leon Escamilla, W.M. Hurng, E.S. Peterson, J.D. Corbett, Synthesis, Structure, and Properties of Ca16Sb11, a Complex Zintl Phase., Inorg. Chem. 36 (1997) 703–710.
- [34] G. Derrien, M. Tillard-Charbonnel, A. Manteghetti, L. Monconduit, C. Belin, Synthesis and Crystal Structure of M11X10 Compounds, M=Sr, Ba and X=Bi, Sb. Electronic Requirements and Chemical Bonding, J. Solid State Chem. 164 (2002) 169–175. doi:10.1006/jssc.2001.9470.
- [35] L. Bin, A. V Mudring, J.D. Corbett, Valence compounds versus metals. Synthesis, characterization and electronic structures of cubic Ae4Pn3 phases in the systems Ae = Ca, Sr, Ba, Eu; Pn = As, Sb, Bi, Inorg. Chem. 42 (2003) 6940–6945.
- [36] L.G. Akselrud, M. Hanfland, U. Schwarz, Refinement of the crystal structure of Bi-II, at2.54 GPa, Zeitschrift Fur Krist. Cryst. Struct. 218 (2003) 415–416.
- [37] G. Bruzzone, E.A. Franceschi, F. Merlo, M5X3 intermediate phases formed by Ca, Sr, and Ba, J. Less-Common Met. 60 (1978) 59–63.
- [38] G. Bergerhoff, R. Hundt, R. Sievers, I.D. Brown, The inorganic crystal structure data base, J. Chem. Inf. Comput. Sci. 23 (1983) 66–69.
- [39] G.W.H. Hohne, W.F. Hemminger, H.J. Flammersheim, Differential Scanning Calorimetry, 2nd Ed., Springer-Verlag, Berlin Heidelberg, 2003.

- [40] J.O. Andersson, T. Helander, L. Hoglund, P.F. Shi, B. Sundman, Thermo-Calc and DICTRA, Computational tools for materials science, Calphad. 26 (2002) 273–312.
- [41] A.V. Vakhobov, Z.U. Niyazova, B.N. Polev, Phase Diagram of the System Sr-Sb, Inorg. Mater. 11 (1975) 306–307.
- [42] S.A. Shukarev, M.P. Morozova, K. Hou-yu, No Title, Zh. Obs. Khim. 27 (1957) 1737.
- [43] T. Lichtenstein, J. Gesualdi, T.P. Nigl, C.T. Yu, H. Kim, Thermodynamic Properties of Barium-Antimony Alloys Determined by Emf Measurements (Accepted Manuscript), Electrochim. Acta. (2017).
- [44] N.D. Smith, J. Soldan-Palma, N. Orabona, C. Marker, S.L. Shang, P. Guan, T. Lichtenstein, J. Gesualdi, T.P. Nigl, Z.K. Liu, H. Kim, Thermodynamic Properties of the Strontium-Antimony Binary System via Experimental and Computational Approaches, Prep. (n.d.).
- [45] C.S. Barrett, P. Cucka, K. Haefner, The Crystal Structure of Antimony at 4.2, 78, and 298K, Acta Crystallogr. 16 (1963) 451–453.
- [46] M. Martinez Ripoll, A. Haase, G. Brauer, The Crystal Structure of Sr2Sb, Acta Crystallogr. 29 (1973) 1715–1717.
- [47] B. Eisenmann, Sr2Sb3, eine Zintl-Phase mit Sb6-Kettenanion, Z. Naturforsch. B. 34 (1979) 1162–1164.
- [48] S.S. Kabalkina, T.N. Kolobyanina, L.F. Vereshchagin, Investigation of the crystal structure of the antimony and bismuth high pressure phases, Sov. Phys. JETP. 31 (1970) 259–263.
- [49] A. Rehr, S.M. Kauzlarich, A New Modification of Sr5Sb3, Acta Crystallogr. 49 (1993) 1442–1444.

- [50] A. Rehr, S.M. Kauzlarich, Sr11Sb10, Acta Crystallogr. 50 (1994) 1859–1861.
- [51] W.M. Hurng, J.D. Corbett, Alkaline-earth-metal antimonides and bismuthides with the A5Pn3 stoichiometry. Interstitial and other Zintl phases formed on their reactions with halogen or sulfur, Chem. Mater. 1 (1989) 311–319.
- [52] K. Deller, B. Eisenmann, SrSb2 eine neue Zintlphase, Z. Naturforsch. B. 31 (1976) 1146– 1147.
- [53] K.W. Ray, Properties of strontium-tin alloys, Ind. Eng. Chem. 22 (1930) 519–522.
- [54] A. Widera, H. Schafer, Das Zustandsdiagramm Sr-Sn und die Verbindung Sr3SnO, J. Less-Common Met. 77 (1981) 29–36.
- [55] D. Marshall, Y.A. Chang, Constitution of the tin-strontium system up to 35 at.% Sr, J. Less-Common Met. 78 (1981) 139–145.
- [56] T.. Okamoto, H., Massalski, Binary Alloy Phase Diagrams, II Edition, 1990.
- [57] F. Zurcher, R. Nesper, S. Hoffmann, T.F. Fassler, Novel arachno-type X56-zintl anions in Sr3Sn5, Ba3Sn5, and Ba3Pb5 and charge influence on zintl clusters, Z. Anorg. Allg. Chem. 627 (2001) 2211–2219.
- [58] A. Palenzona, M. Pani, The phase diagram of the Sr Sn system, 384 (2004) 227–230.
 doi:10.1016/j.jallcom.2004.04.097.
- [59] J. Zhao, Y. Du, L. Zhang, A. Wang, L. Zhou, D. Zhao, J. Liang, Thermochimica Acta Thermodynamic assessment of the Sn – Sr system supported by first-principles calculations, Thermochim. Acta. 529 (2012) 74–79. doi:10.1016/j.tca.2011.11.026.
- [60] E.B. Klebanov, O.. Tvaradze, A.G. Moroachevskii, Activity of Sr in molten alloys with tin, Ysvetn. Met. (1985) 106–107.
- [61] N.D. Smith, Y. Kong, H. Kim, Thermodynamic Properties of Sr-Sn Alloys Determined

via Electromotive Force Measurements, Prep. (n.d.).

- [62] S. Hoffmann, T.F. Fa, SrSn 4 : A Superconducting Stannide with Localized and Delocalized Bond Character, 42 (2003) 8748–8754. doi:10.1021/ic0302128.
- [63] M. Wolcyrz, R. Kubiak, S. Maciejewski, X-Ray investigation of Thermal Expansion and Atomic Thermal Vibrations of Tin, Indium, and Their Alloys, Phys. Status Solidi B Basic Res. (1981).
- [64] T.F. Fassler, S. Hoffmann, SrSn3- A Superconducting Alloy with Non-bonding Electron Pairs, Zeitschrift Fur Anorg. Und Allg. Chemie. 626 (2000) 106–112.
- [65] W. Dorrscheidt, A. Widera, H. Schafer, Dartellung und Kristallstruktur von Sr5Sn3 und Ba5Sn3, Z. Naturforsch. B. 32 (1977) 1097–1099.
- [66] W.J. Boettinger, U.R. Kattner, K.-W. Moon, J.H. Perepezko, Dta and Heat-Flux Dsc
 Measurements of Alloy Melting and Freezing, Methods Phase Diagr. Determ. (2007) 151–
 221. doi:10.1016/B978-008044629-5/50005-7.
- [67] W. Weppner, R.A. Huggins, Thermodynamic Properties of the Intermetallic Systems Lithium-Antimony and Lithium-Bismuth, 125 (1976).
- [68] A. Petric, A.D. Pelton, M.-L. Saboungi, Thermodynamic properties of liquid K-Bi alloys by electromotive force measurements, J. Phys. F Met. Phys. 18 (1988) 1473–1489.
- [69] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack,
 I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P.
 Spencer, M.A. Van Ende, FactSage thermochemical software and databases, 2010-2016,
 Calphad Comput. Coupling Phase Diagrams Thermochem. 54 (2016) 35–53.
 doi:10.1016/j.calphad.2016.05.002.
- [70] A.G. Morachevskii, Lithium–antimony alloys: Phase diagram, thermodynamic properties,

electrochemical behavior in molten and nonaqueous electrolytes, and use in lithium–ion batteries, Russ. J. Appl. Chem. 88 (2015) 1737–1749. doi:10.1134/S10704272150110014.

- [71] M.L. Saboungi, J. Ellefson, G.K. Johnson, W. Freyland, Liquid potassium-antimony alloys: Investigation of some thermodynamic properties, J. Chem. Phys. 88 (1988) 5812–5817. doi:10.1063/1.454540.
- [72] J. Sangster, C.W. Bale, The K-Sn (Potassium-Tin) system, J. Phase Equilibria. 19 (1998)
 67–69. doi:10.1361/105497198770342779.
- [73] W. Gasior, W. Zakulski, Thermodynamic studies and the phase diagram of the Li-Sn system, J. Non. Cryst. Solids. 205-207 (1996) 379–382. doi:10.1016/S0022-3093(96)00446-2.
- [74] C.J. Wen, R.A. Hugglns, Thermodynamic Study of the Lithium-Tin System, (1976).
- [75] T. Lichtenstein, T.P. Nigl, N.D. Smith, H. Kim, Electrochimica Acta Electrochemical deposition of alkaline-earth elements (Sr and Ba) from LiCl-KCl-SrCl 2 -BaCl 2 solution using a liquid bismuth electrode, Electrochim. Acta. 281 (2018) 810–815. doi:10.1016/j.electacta.2018.05.097.
- [76] T.P. Nigl, T. Lichtenstein, Y. Kong, H. Kim, Electrochemical Deposition of Alkaline-Earth Elements (Sr and Ba) from LiCl-KCl Molten Salts Using Liquid Metal Electrodes, Prep. (n.d.).
- [77] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50.
- [78] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter,
 D. Skinner, G. Ceder, The Materials Project: A materials genome approach to accelerating materials innovation, Apl Mater. 1 (2013) 11002.

- [79] Materials Project, (n.d.).
- [80] G. Bergerhoff, I.D. Brown, Inorganic Crystal Structure Database (FIZ Karlsruhe), (1978).
- [81] W.M. Hurng, J.D. Corbett, Alkaline-Earth-Metal Antimonides and Bismuthides with the A5Pn3 Stoichiometry., 1. (1989) 311–319.
- [82] K. Deller, B. Eisenmann, NEW INTERMETALLIC COMPOUND SRSB2,ZEITSCHRIFT FUR Naturforsch. Sect. BA J. Chem. Sci. 31 (1976) 1146–1147.
- [83] S.L. Shang, Y. Wang, D.E. Kim, Z.-K. Liu, First-principles thermodynamics from phonon and Debye model: Application to Ni and Ni3Al, Comput. Mater. Sci. 47 (2010) 1040– 1048.
- [84] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B. 59 (1999) 1758–1775.
- [85] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B. 50 (1994) 17953.
- [86] K. Perdew, J. P., Ruzsinszky, A., Csonka, G. I., Vydrov, O. A., Scuseria, G. E., Constantin, L. A., Zhou, X. & Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, Phys. Rev. Lett. 100 (2008) 136406.
- [87] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B. 13 (1976) 5188–5192.
- [88] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, Ind. Eng. Chem. 40 (1948) 345–348.
- [89] A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD. 15 (1991) 317–425.
- [90] J. Sangster, A.D. Pelton, Bi-Cs (Bismuth-Cesium), Bin. Alloy Phase Diagrams, II Ed.,
 T.B. Massalski. 1 (1990) 730–731.
- [91] S. Fukada, A. Nakamura, Estimation of Melting Points for Some Binary and Tertiary

Fluoride Molten Salts, Fusion Sci. Technol. 66 (2014) 322–336.

[92] H.W. Jenkins, G. Mamantov, D.L. Manning, EMF Measurements on the Nickel-Nickel II couple in Molten Fluorides, Eletroanalytical Chem. Interfacial Electrochem. 19 (1968) 385–389. doi:10.1016/S0022-0728(68)80101-9.

Vita

Nathan Smith was born in Rockville, MD and spent his formative years growing up in Frederick, MD. After graduating from Frederick High School in 2010, Nathan enrolled at the University of Maryland, Baltimore County (UMBC) and also was honored with acceptance into the Honors College as well as the Meyerhoff Scholars Program, which endeavors to increase diversity amongst future leaders in science and engineering. Nathan graduated from UMBC in 2014 with a B.S. in Physics, a B.S. in Mathematics, and a B.A. in Ancient Studies. In the summer of 2014, Nathan joined Dr. Hojong Kim's research group at the Pennsylvania State University. During his graduate studies, Nathan was awarded a Nuclear Engineering University Program fellowship from the Department of Energy which has funded the majority of his research. Despite being exhausted and mildly inebriated as he writes this, Nathan believes that all of this life has generally been worthwhile.

Listed below are his publications during his Ph.D. study:

- 1. Smith, N.D., Lichtenstein, T., Gesualdi, J., Kumar, K., & Kim, H. (2017). Thermodynamic Properties of Strontium-Bismuth Alloys Determined by Electromotive Force Measurements. *Electrochimica Acta*, 225, 584–591.
- 2. Lichtenstein, T., Smith, N.D., Gesualdi, J., Kumar, K., Kim, H. (2017), Thermodynamic properties of Barium-Bismuth alloys determined by emf measurements, *Electrochimica Acta*, 228
- **3.** Kim, H., **Smith, N.D.**, Kumar, K., & Lichtenstein, T. (2016). Electrochemical Separation of Barium into Liquid Bismuth by Controlling Deposition Potentials. *Electrochimica Acta*, 220, 237–244.
- **4.** Nigl, T. P., **Smith, N.D.**, Lichtenstein, T., Gesualdi, J., Kumar, K., & Kim, H. (2017). Determination of thermodynamic properties of alkaline earth-liquid metal alloys using the electromotive force technique. *Journal of Visualized Experiments*, 2017(129), 1–11.
- 5. Kumar, K., Smith, N.D., Lichtenstein, T., & Kim, H. (2018). Electrochemical studies of molten sulfates in LiCl-KCl-Na₂SO₄ at 700 °C. *Corrosion Science*. Vol 133, pp: 17-24.
- **6.** Kumar, K., Gesualdi, G., **Smith, N.D.**, Kim, H. (2018). Influence of gaseous atmosphere on electrochemical behavior of nickel alloys in LiCl-KCl-Na₂SO₄ at 700 °C. *Corrosion Science* vol. 142, pp: 1-11.
- Liu, J., Guan, P., Marker, C., Smith, N.D., Orabona, N., Shang, S., Kim, H., Liu, Z.K. (2019). Thermodynamic properties and phase stability of the Ba-Bi system: A combined computational and experimental study. *Journal of Alloys and Compounds* vol 771, pp: 281-289