CHARACTERIZING DISSOLVED GASES IN CRYOGENIC LIQUID FUELS

By

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

DOCTOR OF PHILOSOPHY

WASHINGTON STATE UNIVERSITY
School of Mechanical and Materials Engineering

JULY 2017

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of IAN A. RICHARDSON find it satisfactory and recommend that it be accepted.

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ACKNOWLEDGMENTS

I have been fortunate to have the incredible support of my family, friends, and colleagues over the last 6 years and I would like to acknowledge several of those people here. I would first like to thank my advisor and mentor, Dr. Jake Leachman. He continued to push me to be a better engineer and a better person. Thank you to my committee Dr. Reid Miller, Dr. Soumik Banerjee, and Dr. Steve Saunders for their expert insight and guidance whenever it was needed.

Dr. Eric Lemmon and Dr. Mark McLinden at NIST taught me everything I know about equations of state and density measurements. I would also like to thank my many mentors at NASA (Dr. Steve Barsi, Dr. Jason Hartwig, Dr. Alok Majumdar, and Dr. Andre Leclair) for their technical discussions and support. I must also thank the NASA Space Technology Research Fellowship program for their financial support through grant number NNX14AL59H. Their staff has been outstanding and a true pleasure to work with over the years.

The HYPER crew was always willing to lend a hand or a listening ear anytime a problem arose, which happened once or twice a week. I would like to thank all of the HYPER members, especially Jake, Chad, Ron, Brandt, Patrick, Eli, Carl, Kevin, and Casey for their technical assistance and friendship. I was also very lucky to find a great group of roommates throughout my graduate career. Thank you to Molly, Allison, Kenny, Alex, and Jesse for the late night discussions and insights from a non-engineering perspective.

Lastly I would like to thank my parents, Mark and Cheryl, siblings, Justin and Emily, and grandparents, Victor and Carrole Buchanan. Their love and encouragement kept me going over the last 6 years. I cannot express how grateful I am. Last but definitely not least I would like to thank Cassie Schultz. I could not have completed this journey without your unwavering love and
support. All of the late night technical discussions and proofreading papers has finally come to an end. I cannot wait to see what the future holds for us.
CHARACTERIZING DISSOLVED GASES IN CRYOGENIC LIQUID FUELS

Abstract

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Pressure-Density-Temperature-Composition (PρT-x) measurements of cryogenic fuel mixtures are a historical challenge due to the difficulties of maintaining cryogenic temperatures and precision isolation of a mixture sample. For decades NASA has used helium to pressurize liquid hydrogen propellant tanks to maintain tank pressure and reduce boil off. This process causes helium gas to dissolve into liquid hydrogen creating a cryogenic mixture with thermodynamic properties that vary from pure liquid hydrogen. This can lead to inefficiencies in fuel storage and instabilities in fluid flow. As NASA plans for longer missions to Mars and beyond, small inefficiencies such as dissolved helium in liquid propellant become significant. Traditional NASA models are unable to account for dissolved helium due to a lack of fundamental property measurements necessary for the development of a mixture Equation Of State (EOS). The first PρT-x measurements of helium-hydrogen mixtures using a retrofitted single-sinker densimeter, magnetic suspension microbalance, and calibrated gas chromatograph are presented in this research. These measurements were used to develop the first multi-phase EOS for helium-hydrogen mixtures which was implemented into NASA’s Generalized Fluid System Simulation
Program (GFSSP) to determine the significance of mixture non-idealities. It was revealed that having dissolved helium in the propellant does not have a significant effect on the tank pressurization rate but does affect the rate at which the propellant temperature rises.

\[ P \rho T \] measurements are conducted on methane-ethane mixtures with dissolved nitrogen gas to simulate the conditions of the hydrocarbon seas of Saturn’s moon Titan. Titan is the only known celestial body in the solar system besides Earth with stable liquid seas accessible on the surface. The \( P \rho T \) measurements are used to develop solubility models to aid in the design of the Titan Submarine. NASA is currently designing the submarine to explore the depths of Titan’s methane-ethane seas to study the evolution of hydrocarbons in the universe and provide a pathfinder for future submersible designs. In addition, effervescence and freezing liquid line measurements on various liquid methane-ethane compositions with dissolved gaseous nitrogen are presented from 1.5 bar to 4.5 bar and temperatures from 92 K to 96 K to improve simulations of the conditions of the seas. These measurements will be used to validate sea property and bubble incipience models for the Titan Submarine design.
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CHAPTER 1 - INTRODUCTION

Two primary research topics were investigated in this work. The effects of pressurizing a traditional liquid hydrogen rocket propellant tanks with gaseous helium is discusses in the first section. In the second section, the research that was conducted to characterize methane-ethane-nitrogen mixtures to support the Titan Submarine is discussed. The layout of the remaining chapters in this dissertation is discussed in the third section.

1.1 Pressurizing Liquid Hydrogen Rocket Propellant Tanks with Gaseous Helium

Though NASA has used helium gas to pressurize liquid hydrogen propellant tanks for decades, little is known about the interactions between helium gas and liquid hydrogen. Traditionally, helium gas is injected into the liquid hydrogen propellant tank to maintain constant tank pressure. This method was used on the Space Shuttle and will continue to be used on the Space Launch System that is under development by NASA. A portion of the gaseous helium dissolves into the liquid hydrogen creating a binary mixture. Predictive models assume that no helium dissolves into the liquid due to a lack of experimental data. This research will improve propellant modelling techniques and provide insight into helium-hydrogen interactions that occur in propellant tanks. This will allow NASA scientists to optimize the design and operation of liquid hydrogen propellant systems.

The objective of this research is to determine if dissolved helium pressurant has a significant effect on the performance of a liquid hydrogen propellant tank. The first experimental Pressure-Density-Temperature-Composition (PpT-x) measurements for cryogenic helium-hydrogen mixtures are presented. The mixture equation of state (EOS) that was developed using
these measurements was used to analyze the self-pressurization rate of a liquid hydrogen tank
assuming the liquid is pure hydrogen and then accounting for dissolved helium in the liquid
hydrogen. The results of this research and recommendations for future work are presented.

1.2 Experimental Measurements of Nitrogen in Liquid Methane-Ethane Mixtures to Support an
Extraterrestrial Submarine for Titan

The hydrocarbon rich seas of Saturn’s moon Titan present an extraordinary opportunity
to explore new worlds and expand our knowledge. With the exception of Earth, Titan is the only
known celestial body in our solar system with stable liquid seas accessible on the surface.
Naturally, NASA is designing an unmanned autonomous submarine to explore these methane-
ethane rich seas with the objective of studying the evolution of hydrocarbons in the universe and
providing a pathfinder for future submersibles.

The seas of Titan are mainly comprised of liquid methane and liquid ethane. The 1.52 bar
nitrogen rich atmosphere of Titan causes significant quantities of gaseous nitrogen to dissolve
into the seas (Hartwig et al., 2016). This creates numerous challenges for a submarine. One of
the key design challenges is accounting for varying compositions of methane and ethane in the
seas and varying amounts of dissolved nitrogen from the atmosphere. Another concern with the
thermal portion of the submarine design is determining under what conditions nitrogen
effervescence will occur and predicting the effects it will have on the submarine operations and
instruments. The solubility and density effects of dissolved nitrogen in liquid methane-ethane
mixtures as well as the conditions under which effervescence will occur in the seas of Titan is
investigated. Video of nitrogen effervescence are provided to better understand the impact of
nitrogen bubbles on the ballast system, scientific instruments, and submarine propellers.
1.3 Dissertation Layout

This dissertation is comprised of a modified conference proceeding paper, manuscripts, and original chapters. Chapter 2 contains an updated version of the published article “Retrofit of a Rubotherm IsoSORP® 2000 for PVT-x and sorption measurements at cryogenic temperatures” (I. A. Richardson, J. W. Leachman, T. M. Blackham, and S. G. Penoncello), reproduced from AIP Conference Proceedings 1573, 1086 (2014), with the permission of AIP Publishing. The paper has been modified to fit into context with the rest of the dissertation and updated to emphasize how the system was used in this research. Elements that were not relevant to this dissertation were removed. Chapter 3 contains the manuscript “Thermodynamic Properties of the Hydrogen-Helium Binary System from 14 K to 33 K at Pressures to 11 MPa” that is being prepared for the Journal of Physical and Chemical Reference Data (T. M. Blackham, I. A. Richardson, J. W. Leachman, and E. W. Lemmon). As the second author on this manuscript, I was responsible for the experimental aspects of this research. This includes the discussion on the motivation for the research, the experimental method, and the experimental measurements presented in sections 3.1, 3.2 and 3.4. Mr. Blackham was the primary researcher on the equation of state development and thus the primary contributor to sections 3.3, 3.5, and 3.6. Having previously developed the equation of state for deuterium (Richardson et al., 2014), I am very knowledgeable in the EOS development and was able to assist Mr. Blackham throughout the development of the equation of state. Though I was not the primary author or contributor to the equation of state development work presented in section 3.5 and section 3.6, I believe this discussion is valuable in that it helps bridge the experimental measurements I conducted in Chapter 3 to the model I developed in Chapter 4. Chapter 4 contains the manuscript “Modelling
the Effects of Dissolved Helium Pressurant on a Liquid Hydrogen Rocket Propellant Tank” that has been submitted to the 2017 Cryogenic Engineering Conference Proceedings (I. A. Richardson and J. W. Leachman). Chapter 5 contains the manuscript “Experimental PpT-x Measurements of liquid Methane-Ethane-Nitrogen Mixtures to Support an Extraterrestrial Submarine for Titan” that is being prepared for Fluid Phase Equilibria (I. A. Richardson, J. W. Hartwig, and J. W. Leachman). Chapter 6 contains the manuscript “Experimental Effervescence and Freezing Point Depression Measurements of Nitrogen in Liquid Methane-Ethane Mixtures to Support an Extraterrestrial Submarine for Titan” that is being prepared for Icarus (I. A. Richardson, J. W. Hartwig, and J. W. Leachman). Chapter 7 contains a discussion of the uncertainties that were considered in the experimental measurements presented in this work. Chapter 8 contains concluding remarks and recommendations for future research.

The units used throughout this dissertation are consistent with the subject matter that is being discussed. In general, the International System of Units is used. For materials specific to NASA research, English units are used as these are the conventional units of NASA. In this work, ‘cryogenic temperatures’ refers to the temperatures ranging from absolute zero to 123.15 K (-150°C) unless otherwise specified.
References


CHAPTER 2 - RETROFIT OF A RUBOTHERM ISOSORP 2000 FOR PVT-X AND SORPTION MEASUREMENTS AT CRYOGENIC TEMPERATURES

2.1 Abstract

A Rubotherm IsoSorp dual-sinker densimeter has been retrofitted to conduct pressure-density-temperature-composition measurements at cryogenic temperatures. Design of a cryostat with vibration-isolation bellows to minimize vibration from the pulse-tube cryocooler is presented. Parasitic heat load calculations are provided to estimate the minimum operating temperature. The system is capable of achieving pressure up to 30 MPa. The design and anticipated capabilities of the experimental system are described.

2.2 Introduction

The current renaissance in aerospace is fueled, at least in part, by the new classes (Type IV and V) of cryogenic compatible composite fuel tanks. Liner-less (Type V) tanks are currently in use with liquid oxygen and liquid nitrogen at pressures up to 41.3 MPa and plans exist to extend use to lower temperature cryogenic mixtures. However, the high operating pressures present new challenges for measurement of sorption into the composite materials and for precision Pressure-Density-Temperature-Composition (PpT-x) measurements of the fluid mixtures. These measurements are necessary for modeling tank degradation, heat transfer at the fluid-tank interface, pressurization, and development of reference quality mixture equations of state (Lemmon and Jacobsen, 1999). PpT-x measurements are the most pressing; the majority of cryogenic mixture property measurements are historical, having not been reviewed in 35 years.
(Hiza et al., 1982). When correlated with a reference quality mixture equation of state, these measurements form the basis for all subsequent system design and modeling.

The retrofit of an established Rubotherm IsoSORP® magnetic suspension balance is presented to address the need for accurate $P\rho T$-x measurements at cryogenic temperatures and elevated pressures. The Rubotherm IsoSORP® instruments utilize a positional magnetic suspension coupling for higher accuracy comparative measurements while maintaining thermal-fluid isolation of the precision micro-balance. Though this dual-sinker densimeter has previously been used for density and sorption measurements (May et al., 2001), only density measurements were conducted in this work. Sorption capabilities for this apparatus have been discussed by Miller et al. (unpublished) and are not discussed in this work. Prior to being retrofitted, the most substantive measurements accomplished by this specific instrument at Washington State University (WSU) were $P\rho T$-x data measured simultaneously with dielectric constants and molar polarizabilities of Methane-Propane-Hexane mixtures over the temperature range from 297–313 K and pressures up to 12 MPa, with uncertainties in densities less than ±0.06 % (May et al., 2001; May et al., 2002).

Modifications to a magnetic suspension balance densimeter for use at cryogenic temperatures are presented. The operational premise of the instrument and subsequent modifications are discussed. Thermal and mechanical design calculations are presented for the modified test cell incorporating a high vacuum cryostat for interface with the vibration isolated cryocooler. The anticipated measurement procedure and capabilities are also provided.
2.3 Modus Operandi

The Rubotherm IsoSORP® 2000 is a gravimetric densimeter utilizing Archimedes’ principle to determine the density of a fluid. Sinkers of known mass and volume are immersed in the fluid and the change in weight reading from the microbalance is used to estimate fluid density. The operating principles for this type of system are well established and similar models are currently in use for designation of primary standards (Wagner and Kleinrahm, 2004; McLinden and Kleinrahm, 2007). A conceptual schematic of the dual-sinker densimeter is shown in Figure 2.1. Custom sinkers of known mass and volume are suspended in a fluid maintained at a fixed temperature and pressure. The sinkers are mechanically coupled to a permanent magnet that has freedom to move vertically. The sinkers and permanent magnet are sealed within the magnetic suspension housing which is subject to the conditions of the fluid being tested. The position of the permanent magnet, and thus the sinkers, are controlled using an electromagnet which is suspended just above the magnetic suspension housing. The electromagnet is then connected to the microbalance. The load applied to the balance has thus been decoupled from the testing conditions due to the separation between the permanent magnet and the electromagnet.
Figure 2.1: Sinker positions for the Zero Point position (I), Measurement Point 1 (II), and Measurement Point 2 (III) are shown for dual-sinker measurements using the Rubotherm IsoSORP®. Components a through n are as follows: a) electromagnet, b) permanent magnet, c) sensor coil, d) magnetic suspension housing, e) magnetic suspension coupling, f) vacuum chamber wall, g) top stainless steel flange, h) stainless steel pipe, i) bottom stainless steel flange, j) G10 thermal barrier, k) copper bus bar to cryocooler, l) sinker 2, m) copper test cell, n) sinker 1.

The position of the permanent magnet is determined by a sensor coil which is used to control the electromagnet. Figure 2.1 depicts dual-sinker operation which uses two sinkers by having two measuring point positions. The system can be used in single-sinker operation by removing sinker 2 and Measurement Point 2.

The Zero Point position, denoted by state (I) in Figure 2.1, is a reference position when both sinkers are resting on a support stand and are not in contact with the suspended permanent magnet and coupling wires. The load transmitted to the balance in Zero Point position is due to the permanent magnet and the suspension wires. The balance is zeroed in this position to eliminate the weight of the permanent magnet and suspension wires from the measurement.
Measurement Point 1, denoted by state (II) in Figure 2.1, is the weighing position when the bottom sinker (sinker 1) is suspended from its support. The load from sinker 1, the permanent magnet, and suspension wiring will be transmitted to the balance through the magnetic coupling. Measurement Point 2, denoted by state (III) in Figure 2.1, is the weighing position when both sinkers are suspended in the fluid. The load measured by the balance will include the load due to sinker 2, sinker 1, the permanent magnet, and the suspension wiring. The measured load will differ from the true weight of the sinkers depending on the density of the fluid they are suspended in. This data can then be used to determine the density of the fluid as discussed by McLinden et al. (2007).

Though this system is capable of dual-sinker operation, it was used for single-sinker measurements in this work because it was only equipped with one hydrogen compatible sinker. For single sinker operation, sinker 2 is removed from the test cell and Measurement Point 2 (position III in Figure 2.1) becomes obsolete. The weighing measurements used to calculate the density are conducted between the Zero Point position and Measurement Point 1 position depicted by state (I) and (II) in Figure 2.1, respectively. The difference in the weight measurement between the Zero Point position and Measurement Point 1 is the weight due to sinker 1. The measured weight will differ from the true mass due to the buoyancy effect of the fluid on the sinker. By knowing the true mass and volume of the sinker, the density of the fluid can be calculated. A detailed discussion of single-sinker densimeters has been done by McLinden et al. (2007) and Wagner and Kleinrahm (2004).
2.4 Retrofitting for Cryogenic Temperatures

A conceptual diagram of the single-sinker densimeter experimental system that was used in this research is shown in Figure 2.2. All components housed within the vacuum chamber that are subject to the fluid conditions were designed to withstand pressures of 30 MPa with a factor of safety of at least 3. The upper pressure limit of the magnetic suspension housing is 30 MPa. Note that the maximum operating pressure decreases to 2 MPa (300 psi) with the addition of the liquid trap featured in Chapters 5 and 6 due to the pressure limit of the Valcor solenoid valve. In order to determine the minimum wall thickness of the internal components, the components were treated as thick-walled, cylindrical pressure vessels (Budynas and Nisbett, 2011). The critical stress occurs in the circumferential direction which is given by the equation

\[
\sigma = \frac{r^2 P_i - r_o^2 P_i + (P_i - P_o) r_i^2 r_o^2 / r^2}{r_o^2 - r_i^2},
\]

where \(\sigma\) is the hoop stress, \(r_i\) and \(r_o\) are the inner and outer radii, \(P_i\) and \(P_o\) are the internal and external pressure, and \(r\) is the radius at the point of interest. Since the maximum stress occurs when \(r = r_o\) and the internal components are under vacuum, Equation 2.1 can be simplified to

\[
\sigma = \frac{2r^2 P_i}{r_o^2 - r_i^2}.
\]

Equation 2.2 was used to determine minimum thicknesses of internal components using the yield stress of the materials and size limitations on the internal diameter. The minimum internal diameter was set to ½ in. to allow sufficient room for the magnetic coupling wire to move without contacting any component. The thermal standoff consists of a ½ inch schedule 40 pipe made of 316 stainless steel welded to two custom flanges made from a 3.5 inch diameter round
bar of 316 stainless steel. The top flange is bolted to the top wall of the vacuum chamber and sealed with a fluorocarbon o-ring while the bottom flange is bolted to the thermal barrier and sealed using 1/16” indium wire. The thermal barrier is made from G10 with dimensions of 3.5 in. diameter and ½ in. thickness. The 316 stainless steel used in the thermal standoff has minimum yield strength of 415 MPa at room temperature. The bus bar and copper test cell are made from C110 H04 copper, having a yield strength of 303.4 MPa.

Figure 2.2: Conceptual diagram of retrofitted Rubotherm.

The internal assembly pictured in Figure 2.3 is enclosed in a 22.5 in. x 10.5 in. x 19.0 in. vacuum chamber made of 304 stainless steel that is capable of achieving a vacuum pressure of 10 E-7 torr so parasitic heat loads due to convection are assumed negligible. Heat transfer due to radiation was mitigated by enclosing the internal assembly in a copper radiation shield that is
covered by 30 layers of multilayer insulation (MLI). Thus, the only heat leak into the test cell considered is conduction through the internal assembly. The thermal standoff pipe was sized to minimize the cross sectional area in which conduction occurs while being able to withstand the pressure requirements and allow enough room for the magnetic suspension wire to pass through unhindered. The G10 thermal barrier separates the thermal standoff from the copper bus bar. However the G10 thermal barrier was found to have little effect on the minimum temperature and was removed after several measurements to ease the assembly process. The test cell was located below the copper bus bar to create a thermal dead end for isothermal temperature measurements as recommended by J. W. Ekin (2006). The copper test cell has a 2.30 in. (30 mm) diameter hole that is 3.937 in. (100 mm) deep. The quartz sinker is connected to the magnetic suspension coupling by a 0.04 in. diameter 316 stainless steel wire. The test cell was modified from the original design to incorporate a ¼ in. stainless steel tube out of the bottom to allow for gas injection into the liquid and liquid extraction for the helium-hydrogen measurements presented in Chapter 3. This was further modified to include a liquid trap for liquid composition measurement for the methane-ethane-nitrogen measurements discussed in Chapter 5.

With radiation and convection assumed negligible, the parasitic heat leak into the test cell was simplified to

\[
 q_{\text{parasitic}} = \frac{T_{\text{room}} - T_{\text{cell}}}{R_{\text{standoff}} + R_{\text{barrier}}},
\]

where \( T_{\text{room}} \) is the temperature of the room, \( T_{\text{cell}} \) is the test cell temperature, \( R_{\text{standoff}} \) is the thermal standoff resistance, and \( R_{\text{barrier}} \) is the thermal barrier resistance. The resistances were calculated using
\[ R = \frac{L}{kA_c}, \]  

(2.4)

where \( L \) is the length of conduction, \( k \) is the integrated average thermal conductivity over the temperature differential, and \( A_c \) is the cross sectional area. The parasitic heat load was calculated to be 2.3 W at 20 K. The minimum temperature occurs when the cooling capacity of the cryocooler is equal to the heat leak due to conduction. A piecewise function of the cooling capacity for a Cryomech PT405 cryocooler was developed based on the manufacturer provided cooling capacity of 0.45 W at 4.2 K and 22 W at 65 K. The lowest achievable temperature was calculated to be 10 K. The actual minimum temperature was found to be approximately 15 K. The discrepancy is likely due to radiation, which was neglected in the initial calculations.

![Figure 2.3: Picture of internal assembly components post machining.](image)
2.5 Instrumentation and Measurement Accuracy

A Paroscientific Digiquartz® pressure transducer with range up to 10,000 psia and accuracy of 1 psia is located upstream of the magnetic suspension housing. Temperature is measured using two Lake Shore GR-1400 secondary standard temperature sensors that are mounted to the bottom and underside of the upper lip of the copper test cell. These germanium RTDs have an accuracy of ± 4 mK at 4.2 K. The temperature is controlled using a resistance heater and a Lake Shore Model 336 temperature controller.

The fused quartz sinker was calibrated at 293.15 K against silicon density standards by the hydrostatic comparator method (McLinden and Splett, 2008). The sinker volume was found to be 27.064847 cm³ with an expanded uncertainty of 5 ppm. The mass was found to be 59.654801 grams with an expanded uncertainty (k=2) of 0.050 mg. The position of the permanent magnet and thus the sinker is controlled by a position sensor and Rubotherm IsoSORP® controller which varies the power to the electromagnet. The weight measurements are conducted using a Mettler Toledo AT261 DeltaRange® microbalance that is accurate to ±10 µg. Similar densimeters are known to consistently produce PρT data with a total uncertainty of 0.01 % to 0.02 % (Wagner and Kleinrahm, 2004).

2.6 Conclusions

A magnetic suspension balance densimeter retrofitted for cryogenic service down to 15 K has been presented. It is believed that this is the first precision single-sinker density instrument capable of continuous operation below 90 K (Richter et al., 2016). This system has been used to

Acknowledgements

This work was funded by the Washington State Joint Center for Aerospace Technology Innovation (JCATI) and Aerojet of GenCorp Inc. The authors thank Dr. Reid Miller of Washington State University (emeritus) for his advice and collaboration in setting up the Rubotherm IsoSORP®. The authors also thank Justin Bahrami and Patrick Gavin for troubleshooting support throughout the assembly.
References


CHAPTER 3 - THERMODYNAMIC PROPERTIES OF THE HYDROGEN-HELIUM BINARY SYSTEM FROM 14 K TO 33 K AT PRESSURES TO 11 MPA

3.1 Abstract

A reduced Helmholtz Equation Of State (EOS) for the thermodynamic properties of parahydrogen-helium binary mixtures and pressure-density-temperature-composition (PρT-x) experimental measurements are presented. The EOS is fit to the new PρT-x measurements along with vapor-liquid equilibrium measurements available in literature. Compilations of the available thermodynamic property measurements and needs for new measurements are presented. An experimental procedure is presented for the PρT-x measurements obtained from a Rubotherm IsoSORP single-sinker densimeter modified for cryogenic service. The PρT-x experimental measurements have expanded uncertainties (k=2) in pressure, temperature, and density of 0.015 MPa, 0.3 K, 0.04 kg m⁻³, respectively. The measureable uncertainty in the composition is less than 0.1 mole %. The thermodynamic property model is valid from 14 K to 33 K and pressures up to 11 MPa. The extrapolation method was based on in-depth property analysis using the Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) and by comparisons to second cross virial coefficients found in literature versus those calculated using the EOS presented. Excellent extrapolation behavior is observed for all second cross virial coefficients from 8 K to 2000 K. The extrapolation range was determined to be to 1000 K and 750 MPa for all compositions.
3.2 Introduction

NASA has used gaseous helium to pressurize liquid hydrogen propellant tanks for decades in order to maintain tank pressure and reduce boil off. This process causes small quantities of helium gas to dissolve into liquid hydrogen creating a cryogenic mixture with thermodynamic properties that vary from those of pure liquid hydrogen. This can lead to inefficiencies in tank performance and instabilities in fluid flow. These small inefficiencies will become significant as NASA plans for longer missions. Traditional propellant models are unable to account for this dissolved helium due to a lack of fundamental property measurements necessary for a mixture Equation Of State (EOS). The first pressure-density-temperature-composition (PρT-x) measurements for the parahydrogen-helium (p-H2He) binary mixture with a corresponding thermodynamic property model are presented.

3.3 Literature Review

Knowledge of the hydrogen-helium binary system is limited to vapor-liquid equilibrium (VLE) phase composition measurements and 2\textsuperscript{nd} virial coefficients (\(B\)). A survey of this literature is provided in Table 3.1.

Table 3.1: Experimental data of hydrogen-helium binary mixtures available in the literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Normal, para, or NS* Exp. Data</th>
<th>No. Points</th>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Composition (H(_2) mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VLE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smith (1952)</td>
<td>NS</td>
<td>131</td>
<td>16.58 – 21.94</td>
<td>0.296 – 5.874</td>
<td>0.966 – 0.998</td>
</tr>
<tr>
<td>Hiza (1972)</td>
<td>Normal</td>
<td>49</td>
<td>19.99 – 28.0</td>
<td>0.091 – 2.062</td>
<td>0.948 – 1.0</td>
</tr>
<tr>
<td>Hiza (1981)</td>
<td>Normal</td>
<td>45</td>
<td>19.99 – 28.0</td>
<td>0.007 – 2.034</td>
<td>0.943 – 1.0</td>
</tr>
<tr>
<td>Streett et al. (1964)</td>
<td>Normal</td>
<td>95</td>
<td>15.50 – 32.50</td>
<td>0.241 – 3.447</td>
<td>0.791 – 0.997</td>
</tr>
<tr>
<td>Sonntag et al. (1964)</td>
<td>99.79 % para-H(_2)</td>
<td>60</td>
<td>20.39 – 31.50</td>
<td>0.0 – 3.454</td>
<td>0.821 – 0.998</td>
</tr>
<tr>
<td>Reference</td>
<td>Type</td>
<td>% para-H₂</td>
<td>T Range</td>
<td>P Range</td>
<td>PΔT Range</td>
</tr>
<tr>
<td>------------------------------</td>
<td>--------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Sonntag et al. (1964)</td>
<td>99.79 % para-H₂</td>
<td>95</td>
<td>15.50 – 32.50</td>
<td>0.241 – 3.447</td>
<td>0.819 – 0.997</td>
</tr>
<tr>
<td>Sneed et al. (1968)</td>
<td>Normal</td>
<td>60</td>
<td>15.50 – 29.80</td>
<td>2.365 –</td>
<td>0.637 – 0.991</td>
</tr>
<tr>
<td>Greene (1966)</td>
<td>NS</td>
<td>19</td>
<td>14.20 – 15.60</td>
<td>0.177 – 1.724</td>
<td>0.995 – 0.999</td>
</tr>
</tbody>
</table>

**Second Virial Coefficient**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type</th>
<th>% para-H₂</th>
<th>T Range</th>
<th>P Range</th>
<th>PΔT Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scholander et al. (1967)</td>
<td>NS</td>
<td>55</td>
<td>20.0 - 74.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brewer et al. (1969)</td>
<td>NS</td>
<td>8</td>
<td>148.16 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Knobler et al. (1959)</td>
<td>NS</td>
<td>1</td>
<td>90.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tanner et al. (1930)</td>
<td>NS</td>
<td>1</td>
<td>298.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gibby et al. (1929)</td>
<td>NS</td>
<td>7</td>
<td>298.19 -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garberoglio et al. (2014)</td>
<td>NS</td>
<td>67</td>
<td>8.0 – 2000.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Denotes Not Specified (NS)

Figure 3.1 shows a complete data map of all current VLE experimental measurements found in the literature. The absence of PpT-x experimental measurements eliminates the ability to optimize the reduced density parameter explained in Section 3.5. Without PpT-x experimental measurements, the deviations in density cannot be found and may cause convergence errors if used as an input parameter to the EOS. Predictive modeling advances since Kunz and Wagner’s 2007 model emphasize the need for a new EOS that uses the full functionality of the Helmholtz energy. Therefore, PpT-x measurements were conducted to compliment the VLE phase composition data to develop a Helmholtz energy based EOS.
Figure 3.1: Data map in pressure-temperature space for VLE experimental measurements found in the literature.

All prior work with the exception of Streett et al. (1964) and Smith (1952) due to the redundancy of the data is presented in Table 3.1. Distinct differences in thermodynamic properties exist between para- and orthohydrogen. Normal hydrogen is defined as a 3:1 mixture of ortho- and parahydrogen. Detailed discussions on ortho- and parahydrogen can be found elsewhere (Leachman et al., 2009). The Sonntag (1964) and Streett (1964) measurements come from the same experimental setup and contain the same measurements although they were published independently with differing ortho-parahydrogen content. The EOS presented in this work uses parahydrogen rather than normal hydrogen as part of the hydrogen-helium binary system. It is assumed that the measurements available in literature were taken on a very high ratio of the para- to orthohydrogen isotope except for the second virial coefficients at the higher temperatures. This assumption is based on the known conversion behavior of ortho- to parahydrogen at cryogenic temperatures. Primary applications for hydrogen-helium mixtures are
at extremely low temperatures with high concentrations of hydrogen. This gives justification for consideration of using parahydrogen rather than normal hydrogen for generating the EOS.

An investigation was conducted in order to resolve any potential discrepancies of using parahydrogen instead of normal hydrogen data while generating the EOS. The Quantum Law of Corresponding States was previously utilized to transform vapor pressure and single-phase densities of parahydrogen to normal hydrogen and orthohydrogen for EOS development (Leachman et al., 2009). In this work, the primary vapor-liquid equilibrium experimental data sets weighted during the optimization process (see Table 3.6) were converted from normal hydrogen temperatures and partial pressures to equivalent parahydrogen temperatures and partial pressures while holding the density unchanged. Equations 3.1 and 3.2 use the relationship between the critical point and triple point (sub-scripts c and t respectively) properties of para and normal hydrogen shown in Table 3.2 to compute the change in the reduced temperature $\Delta T^*$ and partial pressure $\Delta p^*$:

$$
\Delta T^* = \left(\frac{T - T_t}{T_c - T_t}\right) (\Delta T_c^* - \Delta T_t^*) + \Delta T_t^* \quad (3.1)
$$

$$
\Delta p^* = \left(\frac{p - p_t}{p_c - p_t}\right) (\Delta p_c^* - \Delta p_t^*) + \Delta p_t^* \quad (3.2)
$$

Table 3.2: Critical and triple point values for normal and parahydrogen.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Density (mol*dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical point</td>
<td>33.145</td>
<td>1.2964</td>
</tr>
<tr>
<td>Triple point</td>
<td>13.957</td>
<td>0.00736</td>
</tr>
<tr>
<td>Parahydrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical point</td>
<td>32.938</td>
<td>1.2858</td>
</tr>
<tr>
<td>Triple point</td>
<td>13.8033</td>
<td>0.007041</td>
</tr>
</tbody>
</table>
Selected normal hydrogen temperatures and pressures and the equivalent parahydrogen temperatures and pressures for rank one data sets are shown in Table 3.3. An explanation of rank is discussed in section 3.4. The selected normal hydrogen values were chosen to represent low, mid, and high ranged experimentally measured temperatures and pressures. The experimental data sets chosen to be weighted and used in this analysis were made based on the accuracy and precision of the data.

Table 3.3: Selected normal hydrogen vapor-liquid equilibrium experimental data and the transformed equivalent parahydrogen values.

<table>
<thead>
<tr>
<th>Author</th>
<th>Normal hydrogen-helium (original)</th>
<th>Parahydrogen-helium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (K)</td>
<td>P (MPa)</td>
</tr>
<tr>
<td>Streett et al. (1964)</td>
<td>15.500</td>
<td>0.5171</td>
</tr>
<tr>
<td></td>
<td>22.993</td>
<td>2.0684</td>
</tr>
<tr>
<td></td>
<td>30.993</td>
<td>2.8475</td>
</tr>
<tr>
<td></td>
<td>32.492</td>
<td>1.2997</td>
</tr>
<tr>
<td>Sneed et al. (1968)</td>
<td>15.498</td>
<td>5.1780</td>
</tr>
<tr>
<td></td>
<td>25.998</td>
<td>10.3421</td>
</tr>
<tr>
<td></td>
<td>27.798</td>
<td>2.3649</td>
</tr>
<tr>
<td></td>
<td>29.797</td>
<td>3.8611</td>
</tr>
<tr>
<td>Greene (1966)</td>
<td>14.196</td>
<td>0.1793</td>
</tr>
<tr>
<td></td>
<td>15.598</td>
<td>0.2158</td>
</tr>
</tbody>
</table>

The transformed parahydrogen measurements were plotted against the original normal hydrogen measurements in order to conduct an uncertainty analysis during the fitting process. The comparison between the transformed parahydrogen measurements versus the original normal hydrogen measurements had no significant effect on the EOS development when analyzing the entire data set range, i.e. from 14 K to 33 K and up to 11 MPa.
3.4 Experimental Design and PpT-x Measurements

A Rubotherm IsoSORP magnetic suspension densimeter retrofitted for cryogenic service was used to determine fluid densities through the use of Archimedes' principle. The fused quartz sinker was calibrated at 293.15 K against silicon density standards by the hydrostatic comparator method (McLinden and Splett, 2008). The sinker volume was found to be 27.064847 cm$^3$ with an expanded uncertainty of 5 ppm. The sinker mass was found to be 59.654801 grams with an expanded uncertainty ($k = 2$) of 0.050 mg. The operating principles and capabilities of magnetic suspension densimeters are well established, and similar models are currently in use for the designation of primary standards (Wagner and Kleinrahm, 2004; McLinden et al., 2007). A conceptual schematic of the magnetic suspension balance used in this work is shown in Figure 3.2. A detailed explanation of the system can be found in Chapter 2.
Figure 3.2: Conceptual diagram of the retrofitted magnetic suspension densimeter.

The germanium RTD sensors used to determine the fluid temperature are located on the underside of the upper lip and bottom of the test cell and have an accuracy of ± 4 mK. However, this accuracy is never realized due to the heat load through the top of the test cell that creates a thermal gradient between the top and bottom of the test cell. The temperature difference between the bottom and top of the test cell was less than 0.35 K. The reported temperatures are the average of the temperature measurements from the two sensors. The sensors were checked for consistency in liquid nitrogen and liquid helium every 3-6 months to ensure there were no discrepancies between sensors. The accuracy of the pressure transducer was 0.007 MPa. There was also a 0.007 MPa offset pressure accounted for in the reported pressures that was determined by pulling vacuum on the test cell for 24 hours and reporting the minimum pressure reading. This pressure offset was confirmed by direct comparison to a 1000-500A Paroscientific
Intelligent Transmitter with an accuracy of 0.01 %. The offset pressure was present over the applicable pressure range.

A stainless steel tube soldered to the bottom of the test cell was used to extract liquid to obtain the composition measurement. The tubing is plumbed out of the vacuum chamber where a valve is opened allowing the liquid to be pressure fed out of the test cell. The liquid vaporizes as it flows out of the vacuum chamber. The first 5 to 10 seconds of flow was vented before the vapor was collected in a sampling bag. This was done to ensure the gaseous mixture initially in the extraction tube that is not representative of the liquid composition was flush from the lines and to allow sufficient time to flush the barbed connection on the gas sampling bag to ensure air does not get into the bag. One liter multi-layer foil gas sampling bags were used to capture the samples. A minimum absolute pressure of 0.35 MPa was needed to ensure sufficient flow out of the test cell. These samples were analyzed within 24 hours of extraction.

A Varian CP-3800 GC system with a thermal conductivity detector was used to quantify helium and hydrogen gases. The gas chromatograph utilized a Silcosteel HaysSepQ 80/100 mesh packed column (18ft X 0.125in; Supelco). The method used for this analysis incorporated a 10μL stainless steel injection loop controlled by a Valco switching valve installed in the oven. The column oven was held isocratic at 45 °C for 6 min, and the nitrogen carrier gas had a 65 mL/min flow rate (21 psi). Calibrations were made with certified standards (%v/v) of at least four levels for helium (25% up to 75%) and hydrogen (25% up to 100%) that had an absolute uncertainty of ± 0.02 mol %. The reported helium and hydrogen compositions have been normalized so the sum equals 100 percent as the sum of the raw compositions from the gas chromatograph were slightly above or below 100 percent.
The operation of the single-sinker densimeter was validated by conducting measurements of pure liquid parahydrogen. Table 3.4 shows the experimentally measured liquid parahydrogen densities and the percent error of the measured values to those calculated from the parahydrogen equation of state (Leachman et al., 2009). The maximum percent error is 0.1 %. The uncertainty in the parahydrogen EOS in this range is 0.1 %.

Table 3.4: Experimentally measured parahydrogen density values.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Density (kg/m³)</th>
<th>% Error from EOS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.19</td>
<td>0.6067</td>
<td>76.32</td>
<td>0.07</td>
</tr>
<tr>
<td>15.19</td>
<td>0.6081</td>
<td>76.30</td>
<td>0.10</td>
</tr>
<tr>
<td>15.25</td>
<td>0.6522</td>
<td>76.32</td>
<td>0.06</td>
</tr>
<tr>
<td>17.48</td>
<td>1.0011</td>
<td>74.69</td>
<td>0.10</td>
</tr>
<tr>
<td>18.61</td>
<td>0.9315</td>
<td>73.58</td>
<td>0.07</td>
</tr>
<tr>
<td>19.83</td>
<td>1.4796</td>
<td>72.98</td>
<td>0.06</td>
</tr>
<tr>
<td>21.05</td>
<td>1.7568</td>
<td>72.03</td>
<td>0.10</td>
</tr>
<tr>
<td>22.29</td>
<td>2.0402</td>
<td>71.06</td>
<td>0.08</td>
</tr>
<tr>
<td>23.70</td>
<td>2.3759</td>
<td>69.91</td>
<td>0.09</td>
</tr>
<tr>
<td>28.07</td>
<td>3.4267</td>
<td>66.19</td>
<td>0.08</td>
</tr>
<tr>
<td>31.30</td>
<td>4.3003</td>
<td>63.47</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The percent error was calculated using the following equation:

\[
\text{Percent Error} = \left(\frac{\rho_{EOS} - \rho_{measured}}{\rho_{EOS}}\right) \times 100 \tag{3.3}
\]

where \(\rho_{EOS}\) is the density calculated from the parahydrogen equations of state and \(\rho_{measured}\) is the experimentally measured density.

In order to ensure the measurements were conducted on pure parahydrogen, a Fe(OH)\(_3\) (Ionex\textsuperscript{©}) catalyst was placed in the bottom of the test cell and activated by heating the test cell to 320 K and alternating between vacuum and a flow of dry nitrogen gas for 24 hours. Initial measurements were conducted under vacuum over the experimental temperature range to account for the force transmission error (FTE) in the system. This was done again at the end of
the experimental run and averaged to determine the system’s FTE. A detailed discussion of the FTE and fluid density determination for single sinker magnetic suspension densimeters has been done by McLinden et al. (2007). Fluid specific effects were not considered in this work because only one hydrogen compatible sinker was available. The thermal contraction of the quartz sinker was accounted for using the temperature dependent equation for the linear thermal expansion coefficient for fused silica (SRM 739) (Okaji et al., 1995).

Once the catalyst was activated, hydrogen was introduced into the test cell and condensed. A 50 ohm resistance heater connected to a temperature controller was used to fix the temperature of the test cell and thus the fluid. Helium gas was bubbled up through the bottom of the test cell until the desired pressure was reached. It was assumed that this was sufficient mixing to create a homogenous solution. The test cell was then sealed and allowed to achieve steady state. The temperature stabilized within a few minutes but the pressure would take two to three hours to stabilize. Steady state was determined when there was no measurable change in the pressure for at least 30 minutes. Once the fluid had achieved steady state, a density measurement was conducted by taking a series of weighings via the method outlined by McLinden et al. (2007). Seven pressure and temperature measurements were conducted during course of the density measurement. The reported pressures and temperatures are the average of these measurements. A sample of the liquid was then extracted for composition determination. This process was repeated, varying the temperature and pressure, for all of the reported measurements.

Parahydrogen-helium mixture measurements were conducted at pressures of approximately 0.35, 1, and 2 MPa from 16.8 K to 28.9 K. The lower pressure limit was the minimum pressure needed to extract a sample out of the test cell for composition measurements.
The pressure varies slightly at each pressure range due to helium coming out of the liquid solution once the test cell was sealed off and allowed to achieve steady state. The minimum temperature was the coldest the system could achieve for helium-hydrogen mixtures. The upper temperature must be lower than the parahydrogen saturation temperature for the given pressure to ensure the hydrogen was in the liquid state. Measurements were conducted at 4 K increments for target pressures of 1 MPa and 2 MPa, and 3 K increments for the target pressure of 0.35 MPa. The results are shown in Table 3.5. These measurements were used to develop the first parahydrogen-helium binary mixture model that is discussed in the next section.

Table 3.5: Experimental PpT-x measurements of parahydrogen-helium mixtures.

<table>
<thead>
<tr>
<th>Rank</th>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Density (kg/m³)</th>
<th>% He (mol %)</th>
<th>% H₂ (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.8 ±0.3</td>
<td>0.969 ±0.014</td>
<td>76.27 ±0.03</td>
<td>0.75 ±0.09</td>
<td>99.25 ±0.09</td>
</tr>
<tr>
<td>1</td>
<td>20.9 ±0.3</td>
<td>1.089 ±0.015</td>
<td>72.11 ±0.03</td>
<td>1.32 ±0.06</td>
<td>98.68 ±0.06</td>
</tr>
<tr>
<td>1</td>
<td>24.9 ±0.3</td>
<td>1.054 ±0.014</td>
<td>66.56 ±0.03</td>
<td>1.78 ±0.05</td>
<td>98.22 ±0.05</td>
</tr>
<tr>
<td>1</td>
<td>28.9 ±0.3</td>
<td>1.070 ±0.014</td>
<td>58.74 ±0.03</td>
<td>0.74 ±0.07</td>
<td>99.26 ±0.07</td>
</tr>
<tr>
<td>1</td>
<td>16.8 ±0.3</td>
<td>2.130 ±0.014</td>
<td>77.23 ±0.03</td>
<td>1.42 ±0.06</td>
<td>98.58 ±0.06</td>
</tr>
<tr>
<td>2</td>
<td>20.9 ±0.3</td>
<td>2.087 ±0.014</td>
<td>73.98 ±0.03</td>
<td>2.64 ±0.06</td>
<td>97.36 ±0.06</td>
</tr>
<tr>
<td>2</td>
<td>24.9 ±0.3</td>
<td>2.142 ±0.014</td>
<td>69.10 ±0.03</td>
<td>3.62 ±0.06</td>
<td>96.38 ±0.06</td>
</tr>
<tr>
<td>2</td>
<td>28.9 ±0.2</td>
<td>2.097 ±0.014</td>
<td>61.97 ±0.03</td>
<td>3.35 ±0.06</td>
<td>96.65 ±0.06</td>
</tr>
<tr>
<td>1</td>
<td>16.8 ±0.3</td>
<td>0.299 ±0.014</td>
<td>75.36 ±0.03</td>
<td>0.44 ±0.06</td>
<td>99.56 ±0.06</td>
</tr>
<tr>
<td>1</td>
<td>19.9 ±0.3</td>
<td>0.350 ±0.014</td>
<td>71.89 ±0.04</td>
<td>0.29 ±0.06</td>
<td>99.71 ±0.06</td>
</tr>
<tr>
<td>1</td>
<td>22.9 ±0.3</td>
<td>0.372 ±0.014</td>
<td>68.14 ±0.04</td>
<td>0.25 ±0.06</td>
<td>99.75 ±0.06</td>
</tr>
</tbody>
</table>

It is important to note that the reported uncertainties in composition do not account for any uncertainty associated with the liquid extraction technique. The measureable uncertainty for the composition includes the 0.02 mol % uncertainty from the calibration gases used to calibrate the gas chromatograph and the repeatability of the gas chromatograph which was found by conducting multiple composition measurements from a gas sampling bag. The reported
temperature is the average temperature reading from the temperature sensors located on the bottom of the test cell and upper lip of the test cell. Seven temperature recordings were conducted for each sensor during a density measurement for a total of fourteen measurements. The uncertainty accounts for the accuracy of the temperature sensors and the standard deviation of the fourteen temperature measurements. The uncertainty in pressure accounts for the accuracy of the pressure transducer and the standard deviation of the seven pressure readings. The uncertainty in the density measurement accounts for the accuracy of the microbalance, standard deviation of the weighings, and systematic errors associated with magnetic suspension balances. A detailed explanation of the uncertainties can be found in Chapter 7. The reported uncertainties have a coverage factor of 2 ($k = 2$).

3.5 Mixture Model

The GERG-2008 wide-range EOS for natural gases, similar gases, and other mixtures was used as the base model for building the equation of state of the p-H$_2$He binary mixture (Kunz and Wagner, 2012). Equations 3.4 through 3.11 show the GERG-2008 EOS for natural gases and other mixtures. A complete mathematical treatise can be found elsewhere (Kunz and Wagner, 2012).

$$\alpha(\delta, \tau, x) = \alpha^0(\rho, T, x) + \alpha^r(\delta, \tau, x) \tag{3.4}$$

$$\alpha^0(\rho, T, x) = \sum_{i=1}^{N} x_i [\alpha^0_{0i}(\rho, T) + \ln(x_i)] \tag{3.5}$$

The Helmholtz free energy equation ($\alpha$) in its non-dimensional form is represented by equation 3.4 with its corresponding ideal ($\alpha^0$) and residual ($\alpha^r$) constituents. These constituents
can be represented as a function of density, temperature, and composition as shown in equations 3.6, and 3.7.

\[ \alpha_{	ext{r}}(\delta, \tau, x) = \sum_{i=1}^{N} x_i \alpha_{0i}^r(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau) \]  \hspace{1cm} (3.6)  

\[ \alpha_{0i}^r(\delta, \tau) = \sum_{k=1}^{K_{\text{pol}}+{K}_{\text{Exp}}} n_{ol,k} \delta_{ol,k} \tau_{ol,k} + \sum_{k=K_{\text{pol}}+1}^{K_{\text{pol}}+{K}_{\text{Exp}}} n_{ol,k} \delta_{ol,k} \tau_{ol,k} \cdot e^{-\delta_{col,k}} \]  \hspace{1cm} (3.7)  

where \( \alpha_{ij}^r \) and \( \alpha_{0i}^r \) are the residual portions of the reduced Helmholtz free energy, \( x_i \) and \( x_j \) are the mole fraction of the binary components, \( N \) is the number of components in the mixture (in this work \( N = 2 \)), and \( F_{ij} \) is the excess function which can be adjusted as a scaling factor (in this work \( F_{ij} = 1 \)). The pure fluid contributions \( \alpha_{0i}^r \) and \( \alpha_{0i}^r \) use the equations of state given in Leachman et al. (2009) for hydrogen and Ortiz-Vega et al. (2013) for helium.

The reduced mixture density (\( \delta \)) and inverse reduced mixture temperature (\( \tau \)) are expressed as:

\[ \delta = \frac{\rho}{\rho_r(x)} \]  \hspace{1cm} (3.8)  

\[ \tau = \frac{T_r(x)}{T}. \]  \hspace{1cm} (3.9)  

The reduced mixture density and inverse reduced mixture temperature were calculated with equations 3.10 and 3.11, respectively. These equations were determined by fitting binary reducing parameters \( \beta_{v,ij}, \beta_{T,ij}, \gamma_{T,ij}, \) and \( \gamma_{v,ij} \) to experimental measurements.

\[ \frac{1}{\rho_r(x)} = \sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \cdot \frac{x_i + x_j}{\beta_{v,ij} x_i + x_j} \cdot \frac{1}{6} \left( \frac{1}{\rho_{c,i}^2} + \frac{1}{\rho_{c,j}^2} \right)^3 \]  \hspace{1cm} (3.10)  

\[ T_r(x) = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \cdot \frac{x_i + x_j}{\beta_{T,ij} x_i + x_j} \left( T_{c,i} \cdot T_{c,j} \right)^{0.5} \]  \hspace{1cm} (3.11)
The reducing parameters for p-H\textsubscript{2}He were fit using this model and optimized. The coefficients ($n_{ij,k}$) and exponents ($d_{ij,k}$, $t_{ij,k}$, and $c_{ij,k}$) for the p-H\textsubscript{2}He binary mixture are shown in Table 3.6. The reducing parameter values for the p-H\textsubscript{2}He binary mixture are presented in Table 3.7. Qualitative and quantitative assessments were made to ensure the values presented in Tables 3.6 and 3.7 represent the fluid behavior exhibited by the experimental measurements available and that the EOS exhibits correct functional behavior when extrapolated to regions devoid of experimental measurements.

Table 3.6: Coefficients and exponents for the p-H\textsubscript{2}He binary mixture.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$n_{ij,k}$</th>
<th>$t_{ij,k}$</th>
<th>$d_{ij,k}$</th>
<th>$c_{ij,k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.7708</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>-0.08563</td>
<td>1.0</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>-0.2624</td>
<td>1.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.4731</td>
<td>0.4</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 3.7: Reducing parameters for the p-H\textsubscript{2}He binary mixture.

<table>
<thead>
<tr>
<th>$\beta_T$</th>
<th>$\gamma_T$</th>
<th>$\beta_y$</th>
<th>$\gamma_y$</th>
<th>$F_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0736</td>
<td>0.735</td>
<td>1.28</td>
<td>1.232</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Absolute average deviations (AAD) are presented in Table 3.8 for both the thermodynamic property model presented in this work and for Kunz and Wagner’s EOS. The AAD is expressed as

$$
AAD = \frac{1}{n} \sum_{i=1}^{n} |\%\Delta X_i| \tag{3.12}
$$

and

$$
\%\Delta X = \frac{100 \times X_{data} - X_{calc}}{X_{data}} \tag{3.13}
$$
where \( n \) is the number of data points and \( \%\Delta X \) represents the deviations of the experimental measurements from the calculated values. AAD values in conjunction with rank value and composition ranges for each experimental data set categorized by data type are presented in Table 3.8. A rank value of one in Table 3.8 indicates that the data set was weighted during the fitting process and a rank value of 2 indicates the data set was used as supplementary information.

Table 3.8: Parahydrogen-helium binary mixture AAD values.

<table>
<thead>
<tr>
<th>Author</th>
<th>Rank</th>
<th>No. Points</th>
<th>Composition (H₂ mole fraction)</th>
<th>AAD From New EOS (%)</th>
<th>AAD From Previous EOS (%)</th>
<th>No. of Non-converging Points</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>VLE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smith (1952)</td>
<td>2</td>
<td>131</td>
<td>0.966 - 0.998</td>
<td>34.78</td>
<td>75.37</td>
<td>3</td>
</tr>
<tr>
<td>Hiza (1972)</td>
<td>2</td>
<td>49</td>
<td>0.948 - 1.0</td>
<td>15.46</td>
<td>298.05</td>
<td>0</td>
</tr>
<tr>
<td>Hiza (1981)</td>
<td>2</td>
<td>45</td>
<td>0.943 - 1.0</td>
<td>7.74</td>
<td>36.88</td>
<td>0</td>
</tr>
<tr>
<td>Sonntag et al. (1964)</td>
<td>1</td>
<td>95</td>
<td>0.791 - 0.997</td>
<td>14.91</td>
<td>53.65</td>
<td>2</td>
</tr>
<tr>
<td>Sneed et al. (1968)</td>
<td>1</td>
<td>60</td>
<td>0.637 - 0.991</td>
<td>40.80</td>
<td>79.22</td>
<td>6</td>
</tr>
<tr>
<td>Greene (1966)</td>
<td>1</td>
<td>19</td>
<td>0.995 - 0.999</td>
<td>30.05</td>
<td>91.85</td>
<td>0</td>
</tr>
<tr>
<td><strong>Second Virial Coefficient</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scholander et al. (1967)</td>
<td>2</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Brewer et al. (1969)</td>
<td>2</td>
<td>8</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Knobler et al. (1959)</td>
<td>2</td>
<td>1</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tanner et al. (1930)</td>
<td>2</td>
<td>1</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Gibby et al. (1929)</td>
<td>2</td>
<td>7</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Garberoglio et al. (2014)</td>
<td>2</td>
<td>67</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td>1</td>
<td>11</td>
<td>0.964 - 0.997</td>
<td>0.27</td>
<td>0.46</td>
<td>0</td>
</tr>
</tbody>
</table>

*AAD given in cm³/mol for second virial coefficients.
3.6 Results and Discussion

An EOS based on the Helmholtz energy equation was created by Kunz and Wagner and called the “GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures”. The pure fluid EOS for helium and parahydrogen were created after the Kunz and Wagner hydrogen-helium mixture EOS. The new pure fluid equations contribute to the EOS in the $\alpha^0$ and $\alpha^r$ portions of the Helmholtz energy equation. Incorporating the new pure fluid equations of state greatly reduced the deviations in the p-H$_2$He binary mixture of this work.

At the onset of fitting the p-H$_2$He EOS, 85 experimental measurements failed to converge or had very large deviations. In order to achieve an increase in convergence, experimental measurements that initially converged were selected with compositions, temperatures, and pressures similar to non-converging experimental measurements. This was done until only 11 experimental values remained non-converging. Experimental measurements that converged with the previous EOS but did not converge with the EOS presented in this work are due to phase boundary shifts. The shift from the old EOS phase boundary to the new EOS phase boundary caused some experimental measurements to diverge as the points were no longer on the phase boundary. The justification for allowing this to happen is based on the premise that the majority of the experimental data sets correlated well with each other and converged. In the end, more convergence was achieved with the new EOS than with the previously used EOS and there was a significant decrease in AAD as shown in Table 3.8.

During the fitting process the deviations along the vapor side of the saturation line were less than 10 % with a coverage factor of 2. By superimposing the experimental measurements at given compositions, it was determined that the vapor side of the saturation line maintained significantly low deviations whereas the deviations on the liquid side of the saturation line were
extremely high and sporadic. P-H$_2$He is a Type III mixture and the optimization routine was finding only the vapor side root along the saturation line. Figure 3.3 depicts the saturation region for parahydrogen-helium mixtures showing the two roots.

A new routine was needed to find the additional roots for the p-H$_2$He mixture. A new fitting routine was created and added to the optimization process that implemented two additional constraints for VLE experimental measurements. By telling the routine that the binary mixture is a Type III mixture, a constraint making the vapor composition known for a given experimental measurement forces the optimization procedure to find another root. All other roots lie along the liquid side of the saturation curve. This is the first time the Helmholtz energy could be used to directly optimize the liquid phase along the saturation curve. Implementing these constraints to strategic experimental measurements and using the technique of finding convergence one experimental measurement at a time, allowed an EOS to be created that had minimal non-converging measurements with a much greater accuracy along the liquid phase of the saturation line. This development can be generalized to future Type III binary mixtures in order to mitigate the deviations on the liquid side and produce more accurate EOS behavior. A detail discussion of Type III binary mixtures has been done by McHugh et al. (2013).
Prior to this work, no EOS had been created for p-H₂He. The deviations shown in Figures 3.4 and 3.5 for the previous EOS were based on the ideal reduced mixture parameters where $\beta_T$, $\gamma_T$, $\beta_v$, and $\gamma_v$, and $F_{12}$ equal one as presented by Kunz and Wagner (2012). The Kunz and Wagner EOS is ideal for natural gases and other mixtures however, is not suitable for cryogenic mixtures. Therefore, the parameters of the previous EOS by Kunz and Wagner were used as initial guess values to begin generating the new EOS for p-H₂He for this work. Plots similar to Figures 3.4, 3.5, and 3.6 were used to determine strategic experimental measurements to achieve convergence and accurate liquid line calculations during the fitting process.
Figure 3.4: Comparisons of calculated VLE measurements plotted versus temperature for the new p-H2He EOS (top), the previous EOS (middle) to experimental measurements, and the converted equivalent parahydrogen-helium values (bottom).
All VLE and PpT-x experimental measurements available in literature and presented in this work approach the critical point but do not include measurements in the critical region; therefore, no deviations in the critical region are presented.

The vapor phase experimental measurements have an approximate AAD of 10% from 20 K to 31 K for pressures up to 2 MPa. The vapor phase experimental measurement deviations increase from 15 K to 20 K and at pressures below 0.1 MPa. The largest deviations occur at low pressures, circa 0.02 MPa, and at temperatures from 21-23 K. The average uncertainty of the
experimental measurements with a rank of one (see Table 3.8) is 1.09 % for all temperatures and pressures in the vapor phase.

The liquid phase experimental measurements have an approximate average deviation of 15-20 % from 20 K to 30 K for pressure ranging from 2-8 MPa. The liquid phase deviations increase with pressure to approximately 30-40 % as pressures approach 11 MPa. The non-converging measurements are between 27-32 K and pressures greater than 2.5 MPa. The average uncertainty for data sets with a rank of one is 4.24 % for all temperatures and pressures in the liquid phase.

The normal hydrogen and parahydrogen EOS (Leachman et al., 2009) were compared by using the same hydrogen-helium binary EOS reduced parameters and thermodynamic property model to avoid bias. There is an overall 7 % increased uncertainty when using the normal hydrogen EOS versus the parahydrogen EOS. The 7 % average uncertainty held relatively constant at all temperatures, pressures, and compositions with minor fluctuations. Figures 3.4 and 3.5 do not accurately show that 60 experimental measurements did not converge when using the normal hydrogen EOS versus only 37 when using the parahydrogen EOS. In conclusion, parahydrogen was determined to be the best choice in creating an EOS for the hydrogen-helium binary system.

Figures 3.6 and 3.7 show the deviations in density plotted versus pressure and temperature, respectively. The PpT-x deviations of this work range from 0.01 % to 0.66 %. The deviations for the previously used EOS ranged from 0.04 % to 1.56 % as shown in Figures 3.6 and 3.7. Proper binary fluid mixture behavior for the EOS presented in this work was established by plotting all core thermodynamic properties made available by REFPROP (Lemmon et al., 2013) and ensuring correct thermodynamic behavior.
Figure 3.6: Comparison of calculated PpT-x measurements versus pressure for the new P-H2He EOS (top) and previous EOS (bottom) to experimental measurements presented in this work.
Figure 3.7: Comparison of calculated PpT-x measurements versus temperature for the new P-H2He EOS (top) and previous EOS (bottom) to experimental measurements presented in this work.

3.7 Conclusions and Recommendations for Future Research

A reduced Helmholtz EOS for the thermodynamic properties of the parahydrogen-helium binary mixture was presented. The EOS was fit to new PpT-x experimental measurements. An experimental procedure was presented for the PpT-x measurements obtained from a Rubotherm IsoSORP single-sinker densimeter modified for cryogenic service. The thermodynamic property model is valid from 14 K to 33 K and pressures up to 11 MPa. The extrapolation range of the
thermodynamic property model is to 1000 K and 750 MPa for all compositions. The EOS presented significant improvement from what was previously available and a new fitting routine allows Type III mixture optimization along the liquid line of the saturation curve. This new procedure can be implemented for all future Type III binary EOS developments.

Should a wider range of applicability be required, additional VLE and PpT-x experimental measurements should be measured closer to the critical region and at lower temperatures below 15 K with pressures below 1 MPa and above 11 MPa. Such measurements would ease future work of fitting additional cryogenic binary mixtures to the presented thermodynamic model.

3.8 Nomenclature

\( \alpha^r \) Residual part of the reduced Helmholtz free energy (J mol\(^{-1}\))

\( \alpha_{oi}^r \) Residual part of the reduced Helmholtz free energy for component \( i \) (J mol\(^{-1}\))

\( x_i \) and \( x_j \) Mole fraction of the binary components

\( \delta \) Reduced mixture density

\( \tau \) Inverse reduced mixture temperature

\( N \) Number of components in the mixture

\( F_{ij} \) Excess function

\( P \) Pressure (MPa)

\( T \) Temperature (K)

\( \rho \) Density (kg m\(^{-3}\))

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

\( B \) Second virial coefficient

\( n \) Number of data points; also Helmholtz energy coefficients

\( d \) Density exponent
\( t \)  
Temperature exponent

\( c \)  
excess exponent

\( \beta_T \)  
Parameter for reducing temperature

\( \beta_v \)  
Parameter for reducing volume

\( \gamma_T \)  
Parameter for reducing temperature

\( \gamma_v \)  
Parameter for reducing volume

\( K \)  
Helmholtz energy term number

\( AAD \)  
Absolute average deviation

\( X \)  
Relative deviation in experimental properties from calculated values

\( \Delta X \)  
Deviations of the experimental measurements from the calculated values

Acknowledgements

This work was supported by a NASA Space Technology Research Fellowship grant number NNX14AL59H. The authors thank Jonathan Lomber of the Analytical Chemistry Service Center at Washington State University for developing the method to detect helium and hydrogen and calibrating the gas chromatograph. The authors thank Yinglei Han and Alex Dunsmoor for analyzing the composition samples.
References


4.1 Abstract

The self-pressurization of a liquid hydrogen propellant tank was modelled accounting for effects of dissolved helium pressurant in the propellant. For decades NASA has used helium to pressurize liquid hydrogen propellant tanks to maintain tank pressure and reduce boil-off. This process causes helium gas to dissolve into liquid hydrogen creating a cryogenic mixture with thermodynamic properties that vary from pure liquid hydrogen. Traditional NASA models have been unable to account for this dissolved helium due to a lack of fundamental property information. Recent measurements of parahydrogen-helium mixtures enabled the development of the first multi-phase equation of state (EOS) for parahydrogen-helium mixtures. This new EOS has been implemented into NASA’s Generalized Fluid System Simulation Program (GFSSP) to determine the significance of mixture non-idealities. A model was developed for the self-pressurization of a liquid hydrogen propellant tank due to boil-off. The model was run assuming that the liquid propellant was pure liquid hydrogen and assuming helium dissolved into the liquid utilizing the new helium-hydrogen EOS. Having dissolved helium in the propellant does not have a significant effect on the tank pressurization rate but does affect the rate at which the propellant temperature rises.
4.2 Introduction

Helium is typically used to pressurize liquid hydrogen propellant tanks to maintain tank pressure and reduce boil-off. This causes helium gas to dissolve into the liquid hydrogen creating a cryogenic mixture with thermodynamic properties that vary from those of pure liquid hydrogen. This can lead to inefficiencies in fuel storage and instabilities in fluid flow. This has yet to be a major concern because mission durations where liquid hydrogen is the propellant are typically on the order of minutes to a few hours. A cryogenic upper stage has yet to be fired outside of the Earth’s orbit. As NASA plans for longer missions to Mars and beyond, small inefficiencies in propellant storage become significant.

Traditional NASA models have previously been unable to account for the effects of dissolved helium due to a lack of fundamental property measurements necessary for a mixture Equation Of State (EOS). This work builds off of the Pressure-Density-Temperature-Composition (PρT-x) measurements of parahydrogen-helium mixtures that were used to develop the first multi-phase EOS for parahydrogen-helium mixtures presented in Chapter 3. This new EOS was incorporated into NASA’s Generalized Fluid System Simulation Program (GFSSP) software to determine the significance of mixture non-idealities on the bulk tank performance. A simple self-pressurization model of a liquid hydrogen tank was used to compare the effects of dissolved helium on the tank characteristics.

4.3 Self-pressurization Model for a Liquid Hydrogen Tank

The self-pressurization model used in this work was based on NASA’s GFSSP Example 29 “Self-Pressurization of a Cryogenic Propellant Tank Due to Boil-off” (Majumdar et al.,
Example 29 simulates the self-pressurization of a liquid hydrogen tank that was conducted under the Multi-Purpose Hydrogen Test Bed (MHTB) program. A Thermodynamic Vent System (TVS) to help reduce boil-off is investigated in the original problem. The TVS portion of the problem was not used in this work. The self-pressurization of the liquid hydrogen tank was the key focus of this work. A detailed discussion of the tank and the thermodynamic relations used to solve the system can be found in the GFSSP Supplemental Materials for version 701 (Majumdar et al., 2015). A brief overview of the tank and thermodynamic relations used is presented.

The 5083 aluminum tank is cylindrical with a height and diameter of 10 feet. The ends of the tank are elliptical domes. The internal volume is 639 ft$^3$. In order to decrease computational time, the foam insulation and multi-layer insulation (MLI) were eliminated from the model. The radiation load on the tank walls was computed from the original model and then assumed constant over the course of the run. The liquid-vapor interface was modelled as a thin film of zero volume. Figure 4.1 shows the GFSSP model of the settled MHTB tank for a 50% fill level.
The model was kept identical to Example 29 with the exception of the MLI to compare results to the original model and ensure accuracy. The key takeaways of the model shown in Figure 4.1 are that node 4 represents the liquid while nodes 2, 8, 9, 10, and 11 represent the ullage at fill levels of 54 %, 65 %, 80 %, 92 %, and 98 % respectively. The nodes on the left-hand side like nodes 7 and 22 are solid nodes representing the tank wall. The heat transfer between the tank walls and the fluid was computed based on natural convection correlations for a vertical flat plate (Incropera and DeWitt, 1996).
Node 3 acts as a pseudo node to separate the liquid from the ullage. The boundary between the liquid and ullage is modelled as a thin film with no mass or volume. The interface allows mass and heat to exchange between the ullage and liquid volumes as the liquid evaporates. Figure 4.2 shows the terms considered at the interface.

![Diagram of heat and mass transfer across the liquid-vapor interface.](image)

Figure 4.2: Diagram of heat and mass transfer across the liquid-vapor interface.

The ullage contains superheated vapor and pressurant at temperature, \( T_U \). The interface temperature, \( T_I \), is determined by the saturation temperature of the liquid at the ullage pressure. \( T_L \) is the temperature of the liquid and is assumed to be uniform. The evaporative mass is determined using

\[
\dot{m}_v = \frac{Q_{UI} - Q_{IL}}{h_{fg}}
\]  

(4.1)

where \( Q_{UI} \) is the heat transfer from the ullage into the interface, \( Q_{IL} \) is the heat transfer from the interface into the liquid, and \( h_{fg} \) is the enthalpy of vaporization. The heat transfer is a function of the heat transfer coefficient for natural convection, area of the interface, and the respective temperature difference. In order for the model to solve, the heat transfer coefficients had to be set equal to each other based on the thermodynamic properties of the ullage. This is consistent with Example 29 in the GFSSP Supplemental Materials version 701.
In order to determine the effects of dissolved helium pressurant, the model was modified to incorporate helium pressurant in the ullage. The liquid was initially modelled assuming the liquid was pure parahydrogen at -423 °F which corresponds to a saturation pressure of 15.14 psia (Lemmon et al., 2013). The tank was then pressurized to a typical operating pressure of 30 psia with helium pressurant. The composition of the ullage was determined using Dalton’s Law of partial pressures. The ullage was assumed to be an ideal binary mixture of parahydrogen and helium. The model simulation time was 10 hours in order to observe the bulk tank properties.

The model was then modified to incorporate dissolve gaseous helium into the liquid parahydrogen in order to compare the differences. The amount of helium that dissolves in liquid hydrogen was calculated from an empirical solubility model that depends on the total tank pressure and the temperature of the liquid (Zimmerli et al., 2010). For a liquid temperature of -423 °F and total pressure of 30 psia, the corresponding liquid mixture is 0.17 mole % helium – 99.83 mole % parahydrogen. Thermodynamic property tables were created for a mixture of 99.83 mole % parahydrogen – 0.17 mole % helium using the mixture equation of state developed in Chapter 3. The property tables were incorporated into GFSSP to supply the liquid properties. The ullage properties were the same as for the pure liquid hydrogen case. For modelling purposes, the liquid was treated as a pure fluid. The model was solved using the liquid properties corresponding to 99.83 mole % parahydrogen – 0.17 mole % helium.

4.4 Modelling Results

The most critical tank performance metric is the self-pressurization rate as it determines how often the tank must be vented and how much propellant will be lost. This model investigated the pressurization rate with the initial assumption that no helium dissolves in the
propellant and then accounting for 0.17 mole % dissolved helium in the liquid parahydrogen propellant. Both models assume helium pressurant in the ullage and an initial tank pressure of 30 psia. The results are shown in Figure 4.3.

![Self Pressurization of a LH2 Tank](image)

Figure 4.3: Comparison of the self-pressurization rate of a liquid hydrogen propellant tank assuming pure liquid hydrogen propellant (orange x’s) and 0.17 mole % dissolved helium in the liquid (green triangles).

As seen in Figure 4.3 there is no significant difference in the predicted self-pressurization rate of a 30 psia propellant tank when accounting for the dissolved helium pressurant over a ten hour mission. Another tank characteristic that is of interest is the temperature of the propellant as it will affect the density of the liquid and thus the mass flowrate out of the propellant tank. Figure 4.4 shows the temperature of the liquid over a ten hour mission for pure parahydrogen propellant and accounting for 0.17 mole % dissolved helium in the propellant. The GFSSP model predicted a 0.2°F difference in the propellant temperature over the course of the 10 hour mission when accounting for dissolved helium pressurant. The dissolved helium decreases the rate at which the propellant temperature rises.
4.5 Conclusions and Recommendations for Future Research

A self-pressurization of a liquid hydrogen propellant tank was modelled using GFSSP to determine the significance of dissolved helium pressurant in the propellant on the tank performance. It was revealed that dissolved helium pressurant does not have a significant effect on the tank pressurization rate but can slow the rise of the propellant temperature by 0.2 °F over 10 hours. At 30 psia the amount of dissolved helium in liquid hydrogen calculated from the solubility model of Zimmerli et al. (2010) is 0.17 mole %. At 100 psi this increases to 0.89 mole % helium which will increase the effects on the tank performance. Little is known about the effects of dissolved helium and helium effervescence in liquid hydrogen as it pertains to rocket
engines. Additional research is needed to determine when dissolved helium will come out of solution in liquid hydrogen and what effects it will have on subsequent systems.

While developing the self-pressurization model, it was discovered that the largest uncertainty in the pressurization rate was due to the uncertainty in the heat transfer coefficients, not the amount of dissolved helium as initially suspected. The heat transfer coefficients that were used in this model are based on generic natural convection correlations. These correlations contain constants that were determined based on traditional fluids. Liquid hydrogen and saturated hydrogen vapor will behave much differently than traditional fluids due to the quantum nature of the molecules at cryogenic temperatures. The uncertainty in the heat transfer coefficients for liquid hydrogen and saturated hydrogen vapor is not well known. Thus far in the history of space travel these uncertainties have not been an issue because the durations of missions utilizing liquid hydrogen have been on the order of minutes to a few hours. As humanity looks to expand mission durations to days or weeks, these uncertainties will become significant and will need to be addressed if liquid hydrogen will continue to be used as a propellant.

It is important to note that the solubility model used in this work is based on steady state conditions. It does not account for transport properties associated with helium in liquid hydrogen. Experiments conducted on NASA’s Evolvable Cryogenics (eCryo) Engineering Design Unit (EDU) tank (Stephens, 2016) and the PpT-x measurements discussed in Chapter 3 revealed that helium pressurant injected into liquid hydrogen will slowly degas from the liquid causing the tank pressure to rise. This phenomenon will be discussed in detail in Chapter 8.

The transport properties of helium-hydrogen mixtures and the rate at which helium dissolves in or degasses from liquid hydrogen has not been studied. Additional experiments
should be conducted to further investigate the transport properties of helium-hydrogen mixtures. Injecting helium into the liquid should be avoided whenever possible.

Acknowledgements

The authors would like to thank Alok Majumdar and Andre Leclair from the Marshall Space Flight Center for their assistance setting up the GFSSP model. This work was supported by NASA Space Technology Research Fellowship grant NNX14AL59H.
References


CHAPTER 5 - EXPERIMENTAL $PρT-x$ MEASUREMENTS OF LIQUID METHANE-ETHANE-NITROGEN MIXTURES TO SUPPORT AN EXTRATERRESTRIAL SUBMARINE FOR TITAN

5.1 Abstract

Twenty-two Pressure-Density-Temperature-Composition ($PρT-x$) measurements are presented from 92 K to 96 K for pressures from 1 bar to 4.5 bar for varying compositions of methane, ethane, and nitrogen. These measurements are being used to aid in the design of the Titan Submarine that NASA is designing to explore the hydrocarbon rich seas of Saturn’s moon Titan. Titan is the only celestial body in our solar system with stable liquid lakes and seas on its surface other than Earth. The thermodynamic properties of Titan’s seas have not been well characterized. The solubility of nitrogen for varying methane-ethane compositions and the effects of dissolved nitrogen on the density of the seas are investigated.

5.2 Introduction

Titan presents a unique opportunity to advance our knowledge and capability to explore new worlds. This moon of Saturn is the only celestial body in our solar system, other than Earth, that has stable liquid seas, rivers, and a hydrological cycle similar to Earth. The key difference is that the hydrological cycle of Titan is based on methane and the seas of Titan consist of primarily liquid ethane and methane. Data from Cassini indicates that the atmosphere is comprised of 95 % gaseous nitrogen with an atmospheric pressure of 1.5 bar and surface temperature of 93 K. Titan’s hydrocarbon seas are able to absorb a significant amount of
nitrogen from the atmosphere causing significant uncertainty in the thermodynamic properties of
the seas (Hartwig et al., 2016).

NASA is designing an unmanned submarine to explore Titan and gain insight into
extraterrestrial seas and expand NASA’s capabilities of planetary exploration to include
autonomous nautical operations (Oleson, 2014). The submarine must operate autonomously,
study atmosphere/sea exchange, interact with the seabed, hover at the surface and at any depth
within the sea, and be capable of tolerating variable hydrocarbon compositions. One of the key
challenges in the submarine design is accounting for variations in the methane and ethane
composition in the seas as well as the dissolved gaseous nitrogen from the atmosphere. The
solubility and density effects of dissolved nitrogen in liquid methane-ethane mixtures relevant to
Titan are investigated.

5.3 Experimental System

The Pressure-Density-Temperature-Composition (P\(p_T\)-x) measurements were conducted
using a magnetic suspension densimeter utilizing Archimedes’ principle that has been retrofitted
for cryogenic service. This experimental system has been previously used for other cryogenic
mixtures and a detailed discussion of the operation can be found in Chapters 2 and 3. The core
components of the experimental system are a cryostat, magnetic suspension balance, test cell to
condense methane-ethane mixtures, and liquid trap which is used to determine the composition.
A conceptual schematic of the experimental system is shown in Figure 5.1. Two density
measurements were conducted on pure methane at 92.1 K and 0.3 bar (4 psia) to validate the
accuracy of the densimeter. The measured densities agreed with the methane equation of state
within 0.006 \(\%\), well within the EOS uncertainty of 0.05 \(\%\) (Kunz et al., 2007).
Cylinders of 99.99% pure methane and 99.99% pure ethane were mixed in a mixing tank based on Dalton’s law of partial pressures to achieve the desired composition. The gaseous mixture is then condensed in the test cell via cryo-pumping to simulate the Titan seas. Nitrogen gas is then flowed in through the liquid trap until the desired pressure is achieved to simulate Titan’s nitrogen-rich atmosphere. Temperature sensors were located on the test cell and liquid trap. Resistance heaters located on the copper test cell and bus bar were used to control the temperature of the test cell and liquid trap to achieve thermal equilibrium. Once the desired temperature and pressure was achieved, the system was sealed and allowed to come to steady state. Steady state was determined when there was no measureable change in the temperature or pressure. The system would take several hours to achieve steady state after the test cell had been
sealed. It was assumed that there was no stratification between the liquid in the test cell and the liquid trap due to the uniform pressure and temperature and the significant mixing that occurs during the nitrogen bubbling process. Once steady state was achieved, a density measurement was conducted following the procedure outlined by McLinden et al. (2007). Seven temperature and pressure measurements were recorded over the course of the density measurement. The reported values are the average of each measurement.

After the pressure, density, and temperature measurements were recorded, the normally open solenoid valve was actuated to capture a liquid sample for the composition measurement. The liquid was heated until it was above the saturation temperature of ethane since ethane has the highest saturation temperature of the three components. This ensured that every component in the mixture was vaporized. The vapor from the liquid trap was collected in a sampling cylinder where it is later extracted and analyzed using a Varian CP-3800 GC system with a thermal conductivity detector (TCD) and flame ionization detector (FID). The TCD was used to determine the quantity of nitrogen and the FID determined the quantity of methane and ethane. The system was calibrated with certified standards (%v/v) prepared by ISGAS of at least three levels for nitrogen (5 % up to 20 %), methane and ethane (15 % up to 100 %) having a certified accuracy of 5 mole %. The uncertainty associated with the certified gas standards and calibration curve was not accounted for in the reported composition uncertainties. The only error considered in the reported composition uncertainties is the standard deviation from conducting multiple composition measurements from one or more gas sampling bags for each data point and the error associated with the vapor headspace on the extraction tube from the liquid trap. The composition accuracy reported in Table 5.1 was founding using the largest reported uncertainty. A detailed
explanation of the liquid trap is presented in Chapter 6. The sensors and instruments used to conduct the \( P \rho T \)-x measurements have been provided in Table 5.1.

Table 5.1: Instruments and sensors used over the course of the reported \( P \rho T \)-x measurements.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Instrument</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Paroscientific Digiquartz Transducer Model 1000-500A</td>
<td>0.0035 bar</td>
</tr>
<tr>
<td></td>
<td>Paroscientific Digiquartz Transducer Model 410K-101</td>
<td>0.07 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>Lakeshore GR-1400 Germanium RTD</td>
<td>±0.018 K</td>
</tr>
<tr>
<td></td>
<td>Cryo-con S950-BB Silicon Diode (calibrated)</td>
<td>±0.2 K</td>
</tr>
<tr>
<td></td>
<td>Cryo-con S950-BB Silicon Diode (uncalibrated)</td>
<td>±0.4 K</td>
</tr>
<tr>
<td>Mass</td>
<td>Mettler Toledo AT261 DeltaRange Balance</td>
<td>10 µg</td>
</tr>
<tr>
<td>Composition</td>
<td>Varian CP-3800 GC</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

Throughout the course of these measurements, three different temperature sensors and two pressure transducers were used. This was due to sensors breaking or malfunctioning. The sensors with the highest accuracy were utilized whenever possible. A detailed discussion of the uncertainties can be found in Chapter 7.

5.4 Measurement Results

A review of binary and ternary methane, ethane, and nitrogen measurements has previously been done by W. R. Thompson (1985). This work provides targeted methane-ethane-nitrogen \( P \rho T \)-x measurements relevant to Titan’s seas to fill gaps in the literature. The temperature was varied from 92 K to 96 K and the pressures were varied from 1 bar to 11 bar to account for varying sea depths. The pressure-density-temperature-composition measurements
and their respective uncertainties are presented in Table 5.2. All reported uncertainties have a coverage factor of 2.

Table 5.2: Methane-ethane-nitrogen P,T,x measurements.

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Temperature [K]</th>
<th>Pressure [bar]</th>
<th>Density [kg/m³]</th>
<th>Methane [mol %]</th>
<th>Ethane [mol %]</th>
<th>Nitrogen [mol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.0 ±0.4</td>
<td>1.383 ±0.007</td>
<td>650.5 ±0.5</td>
<td>-</td>
<td>96.7 ±0.1</td>
<td>3.3 ±0.1</td>
</tr>
<tr>
<td>2</td>
<td>92.0 ±0.4</td>
<td>10.394 ±0.008</td>
<td>651.3 ±0.3</td>
<td>-</td>
<td>95.2 ±0.2</td>
<td>4.8 ±0.2</td>
</tr>
<tr>
<td>3</td>
<td>92.0 ±0.4</td>
<td>1.591 ±0.007</td>
<td>451.0 ±0.3</td>
<td>88.4 ±0.1</td>
<td>-</td>
<td>11.6 ±0.1</td>
</tr>
<tr>
<td>4</td>
<td>92.1 ±0.8</td>
<td>2.737 ±0.009</td>
<td>586.4 ±0.1</td>
<td>29.1 ±0.1</td>
<td>54.5 ±0.1</td>
<td>16.4 ±0.1</td>
</tr>
<tr>
<td>5</td>
<td>92.1 ±0.8</td>
<td>2.760 ±0.009</td>
<td>491.1 ±0.1</td>
<td>82.6 ±0.3</td>
<td>9.3 ±0.7</td>
<td>8.1 ±0.5</td>
</tr>
<tr>
<td>6</td>
<td>92.1 ±0.8</td>
<td>2.785 ±0.008</td>
<td>471.2 ±0.1</td>
<td>87.9 ±0.1</td>
<td>5.4 ±0.1</td>
<td>6.7 ±0.1</td>
</tr>
<tr>
<td>7</td>
<td>92.1 ±0.8</td>
<td>10.988 ±0.011</td>
<td>527.2 ±0.1</td>
<td>60.1 ±0.2</td>
<td>29.3 ±0.2</td>
<td>10.6 ±0.2</td>
</tr>
<tr>
<td>8</td>
<td>92.1 ±0.8</td>
<td>11.005 ±0.010</td>
<td>478.3 ±0.1</td>
<td>75.2 ±0.2</td>
<td>6.2 ±0.2</td>
<td>18.6 ±0.2</td>
</tr>
<tr>
<td>9</td>
<td>94.0 ±0.8</td>
<td>2.74 ±0.14</td>
<td>569.7 ±0.1</td>
<td>40.5 ±0.1</td>
<td>50.6 ±0.1</td>
<td>8.8 ±0.1</td>
</tr>
<tr>
<td>10</td>
<td>94.0 ±0.4</td>
<td>2.764 ±0.008</td>
<td>455.1 ±0.2</td>
<td>68.0 ±0.1</td>
<td>19.3 ±0.1</td>
<td>12.7 ±0.2</td>
</tr>
<tr>
<td>11</td>
<td>94.0 ±0.8</td>
<td>5.43 ±0.14</td>
<td>614.6 ±0.1</td>
<td>20.6 ±0.1</td>
<td>61.8 ±0.2</td>
<td>17.6 ±0.2</td>
</tr>
<tr>
<td>12</td>
<td>94.0 ±0.4</td>
<td>5.685 ±0.008</td>
<td>475.3 ±0.3</td>
<td>72.4 ±0.1</td>
<td>10.6 ±0.1</td>
<td>16.9 ±0.1</td>
</tr>
<tr>
<td>13</td>
<td>94.0 ±0.4</td>
<td>5.687 ±0.009</td>
<td>517.3 ±0.3</td>
<td>62.0 ±0.1</td>
<td>24.4 ±0.1</td>
<td>13.6 ±0.1</td>
</tr>
<tr>
<td>14</td>
<td>94.0 ±0.4</td>
<td>8.281 ±0.008</td>
<td>474.7 ±0.1</td>
<td>75.7 ±0.2</td>
<td>8.2 ±0.1</td>
<td>16.2 ±0.1</td>
</tr>
<tr>
<td>15</td>
<td>94.0 ±0.4</td>
<td>10.976 ±0.009</td>
<td>606.8 ±0.1</td>
<td>41.1 ±0.3</td>
<td>15.9 ±0.3</td>
<td>42.9 ±0.2</td>
</tr>
<tr>
<td>16</td>
<td>95.0 ±0.1</td>
<td>1.151 ±0.007</td>
<td>525.0 ±0.2</td>
<td>65.5 ±0.6</td>
<td>26.2 ±0.2</td>
<td>8.3 ±0.8</td>
</tr>
<tr>
<td>17</td>
<td>96.0 ±0.8</td>
<td>1.06 ±0.14</td>
<td>607.5 ±0.1</td>
<td>17.7 ±0.1</td>
<td>80.3 ±0.1</td>
<td>2.0 ±0.1</td>
</tr>
<tr>
<td>18</td>
<td>96.0 ±0.8</td>
<td>1.64 ±0.14</td>
<td>565.3 ±0.1</td>
<td>48.0 ±0.1</td>
<td>45.8 ±0.1</td>
<td>6.2 ±0.1</td>
</tr>
<tr>
<td>19</td>
<td>96.0 ±0.4</td>
<td>2.763 ±0.008</td>
<td>471.0 ±0.2</td>
<td>79.4 ±0.1</td>
<td>18.2 ±0.1</td>
<td>2.4 ±0.1</td>
</tr>
<tr>
<td>20</td>
<td>96.0 ±0.4</td>
<td>11.081 ±0.009</td>
<td>521.5 ±0.3</td>
<td>56.9 ±0.2</td>
<td>20.6 ±0.2</td>
<td>22.5 ±0.2</td>
</tr>
<tr>
<td>21</td>
<td>96.0 ±0.4</td>
<td>11.088 ±0.009</td>
<td>472.5 ±0.4</td>
<td>68.6 ±0.2</td>
<td>6.7 ±0.2</td>
<td>24.7 ±0.2</td>
</tr>
</tbody>
</table>
The discrepancies in the uncertainty of the temperature and pressure measurements are due to the use of several different sensors as discussed in the Section 5.3. The general trend of the measurements is that the solubility of nitrogen increases with increased pressure, increased mole fraction of methane, and decreased temperature. Measurements 4 and 19 do not agree with this trend. One explanation for this deviation from the trend is that there was leakage through the solenoid valve, biasing the composition, which went undetected by the experimenter.

The saturation pressure of nitrogen at 92 K, 94 K, and 96 K is 4.3 bar, 5.0 bar, and 5.8 bar, respectively. Thus measurements 2, 7, 8, 11-15, 20 and 21 were conducted at pressure above the saturation pressure of nitrogen. This led to larger nitrogen compositions than would be expected from gaseous diffusion.

5.5 Conclusions

Twenty-one pressure-density-temperature-composition measurements on methane-ethane-nitrogen mixtures relevant to Saturn’s moon Titan have been reported. It is shown that density increases with increased pressure, decreased temperature, increased mole fraction of ethane, and increased mole fraction of nitrogen. The data shows that the solubility of nitrogen is 3 to 4 times greater in liquid methane than liquid ethane at the approximate atmospheric pressure of Titan (1.5 bar) and 93 K. The solubility of nitrogen increases with increased pressure, decreased temperature, and increased mole fraction of methane. The reported measurements have been implemented in an analytical solubility model to aid in the design of the Titan Submarine (Hartwig et al., 2017).
Acknowledgements

The authors would like to thank Jonathan Lomber and Alex Dunsmoor of Washington State University for conducting the methane-ethane-nitrogen composition measurements. This work was supported by NASA Space Technology Research Fellowship grant NNX14AL59H and NASA research grant NNC16MF93P.
References


6.1 Abstract

NASA is designing an unmanned submarine to explore the depths of the hydrocarbon-rich seas on Saturn’s moon Titan. Data from Cassini indicates that the Titan polar environment sustains stable seas of variable concentrations of ethane, methane, and nitrogen, with a surface temperature near 93 K. The submarine must operate autonomously, study atmosphere/sea exchange, interact with the seabed, hover at the surface or any depth within the sea, and be capable of tolerating variable hydrocarbon compositions. Currently, the two main thermal design concerns are the effect of effervescence on submarine operation and the effect of unknown property variation with depth, both of which affect submarine ballast system, science instruments, and propellers. Effervescence measurements on various liquid methane-ethane compositions with dissolved gaseous nitrogen are thus presented from 1.5 bar to 4.5 bar at temperatures from 92 K to 96 K to simulate the conditions of the seas. After conducting twelve effervescence measurements, two freezing point depression measurements were conducted. The freezing liquid line was depressed more than 15 K below the triple point temperatures of pure ethane (90.4 K) and pure methane (90.7 K). These experimental effervescence measurements will be used to validate sea property and bubble incipience models for the Phase 2 Titan Submarine design.
6.2 Introduction

Saturn’s moon Titan is the only known celestial body in our solar system besides Earth with stable liquid seas accessible on the surface. NASA is currently designing an unmanned autonomous submarine to explore these methane-ethane rich seas: 1) to study the evolution of hydrocarbons in the universe, 2) to study Titan’s geology (atmosphere/sea exchange, surface, shore, waves, heat transfer), and 3) to provide a pathfinder for later designs of submersibles in the seas hidden beneath the ice crust of other outer planetary moons (Hartwig et al., 2016). The two main thermal design concerns are determining how dissolved nitrogen gas will affect the operation of the submarine and instruments as well as determining the effect of unknown sea property variations with depth on submarine operation.

Data from Cassini indicates that the surface temperature of Titan is 93 K with an atmospheric pressure of 1.5 bar. Unlike the liquid water oceans of Earth, the hydrocarbon seas of Titan are able to absorb a relatively substantial amount of nitrogen from the atmosphere, causing gaseous nitrogen to go into solution. The solubility of nitrogen varies drastically depending on the composition of ethane and methane in the seas, which can vary from nearly pure ethane in Kraken Mare to 74 mol % methane in Ligeia Mare (Hartwig et al., 2016). At Titan’s surface conditions of 93 K and 1.5 bar, the solubility of nitrogen in Ligeia Mare is 13 mol % while the solubility of nitrogen in Kraken Mare is just 3 mol % (Hartwig et al., 2017). This range in solubility presents several design challenges and creates uncertainty regarding ice formation in the seas due to Titan’s surface temperature being within 2 K to 3 K of the triple point of pure methane and ethane. Though there is limited experimental data, the literature suggests that significant freezing point depression can be achieved and that the buoyancy of the ice will
depend on the solubility of nitrogen and the methane-ethane composition of the sea (e.g. Thompson, 1985; Roe and Grundy, 2012; Prokhvatilov and Yantsevich, 1983; Hofgartner and Lunine, 2013).

One of the primary design challenges with the thermal portion of the submarine is predicting the effects of nitrogen effervescence on submarine operation. Waste heat from the submarine radioisotope power system may cause dissolved nitrogen gas to come out of solution. In a quiescent case, bubbles may interfere with sensitive science measurements. In a moving case, bubbles that form along the body may coalesce at the aft end of the submarine and cause cavitation in the propellers.

This work investigates the heat loads and surface temperatures at which nitrogen gas begins to come out of solution to determine the point of bubble incipience as a function of sea temperature, pressure, and liquid methane-ethane compositions. Videos of effervescence were taken to better understand the impact that nitrogen gas bubbles may have on the scientific instruments, ballast systems, and submarine propellers. Additionally, two freezing point depression measurements were conducted on methane-ethane-nitrogen mixtures to determine the degree of depression.

6.3 Experimental Design

The effervescence measurements presented in this work were completed by modifying the cryogenic densimeter system discussed in Chapters 2. The key components of the system include a custom cryostat and test cell to condense methane-ethane mixtures, video camera with a borescope, cartridge heater to simulate waste heat from the submarine, and liquid trap which is
used to determine the composition. A schematic of the experimental system is shown in Figure 6.1.

Airgas cylinders of 99.99 % pure ethane and 99.99 % pure methane were mixed based on partial pressure in a mixing tank to achieve the desired composition. The gaseous mixtures were then condensed via cryo-pumping in the copper test cell where nitrogen was bubbled in through the liquid trap at the bottom until the desired pressure was achieved. Nitrogen bubbling was a turbulent process ensuring that the liquid mixture within the liquid trap and test cell was well mixed. Once the temperature and pressure of the simulated sea was stable, the cartridge heater
was turned on to simulate the heat load from the submarine. A summary of the sensors and instruments used to conduct the effervescence measurements is presented in Table 6.1.

Table 6.1: Summary of instrumentation and sensors used to conduct effervescence measurements.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Instrument</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Paroscientific Digiquartz®</td>
<td>0.01 %</td>
</tr>
<tr>
<td></td>
<td>Pressure Transducer Model 1000-500A</td>
<td></td>
</tr>
<tr>
<td>Sea Temperature</td>
<td>LakeShore PT-100</td>
<td>±0.25 K</td>
</tr>
<tr>
<td>Heater Surface</td>
<td>Cryo-con S950-BB (uncalibrated)</td>
<td>±0.4 K</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>Varian CP-3800 GC</td>
<td>0.6 %</td>
</tr>
<tr>
<td>Heat Flux</td>
<td>HP 6438B DC Power Supply</td>
<td>±0.25 V, ±0.025 A</td>
</tr>
</tbody>
</table>

The temperature of the liquid was measured using a temperature rake which consists of four platinum resistance thermometers (PRT) spaced approximately 2.5 cm apart. Two PRTs were located below the cartridge heater and two PRTs were above the heater. The bulk sea temperature was determined by averaging the two PRT measurements that were below the heater which generally agreed within 0.1 K. The PRTs above the heater were used to measure the thermal gradient that occurred above the heater due to natural convection. The temperature of the test cell and liquid were controlled using a resistance heater and Proportional Integral Derivative (PID) temperature controller.
The submarine was represented by a 5 cm long, 0.76 cm diameter cartridge heater. The heater surface temperature was measured by a silicon diode that was thermally anchored to the flat end of the heater. The power supplied to the heater was controlled using a DC power supply. Initial measurements were conducted at near steady state conditions by increasing the heater power in 2 volt increments and waiting at least 5 minutes until the sea and heater temperature stabilized. If effervescence did not occur, heater power was increased in 2 volt increments until effervescence occurred. Later measurements were conducted by increasing the heater power rapidly; 2 volts every 30 seconds until effervescence occurred to minimize the effect of trace amounts of non-visible, dissolved gas coming out of solution during the progression towards effervescence. Additional information on the two measurement methods is provided in Section 6.4.

Effervescence was detected optically using a video camera and borescope. The borescope allowed the video lens to pass into the test cell and maintain a hermetic seal. As a result the end of the borescope was subject to the condition of the fluid being measured. This led to poor resolution for a few of the measurements due to fogging. A large uncertainty in the effervescence measurements is determining when effervescence occurs; similar to the different boiling regimes, there are varying degrees of effervescence. Effervescence was determined at the point of visible bubbles consistent within the detection limits of the camera.

The composition of the liquid mixture at effervescence was obtained using a liquid trap. The liquid trap consisted of a section of brass pipe connected to the test cell through a ¼ inch copper tube. A normally open solenoid valve was located between the test cell and the brass pipe allowing liquid to move freely between the liquid trap and the test cell. It was assumed that there was no stratification between the liquid in the test cell and the liquid trap because of the
turbulence caused by nitrogen bubbling. Once effervescence occurred, the solenoid valve was closed separating the liquid in the trap from the liquid in the test cell. The liquid in the liquid trap was heated until it was completely vaporized. Vaporization is ensured by heating the liquid trap above the saturation temperature of liquid ethane, which is the highest of the three components. The vapor was collected in a sampling cylinder. After the liquid was completely vaporized, the gaseous mixture was extracted and collected in a 1 liter multilayer gas sampling bag where it was analyzed via gas chromatography. For redundancy, often two separate gas sampling bags were filled and analyzed for the composition. A Varian CP-3800 GC system with a thermal conductivity detector was used to quantify nitrogen and a flame ionization detector was used to quantify the methane and ethane gases. The gas chromatograph utilizes a Silcosteel HaysSepQ 80/100 mesh packed column (18ft X 0.125in; Supelco). The method used for this analysis incorporated a 10μL stainless steel injection loop controlled by a Valco switching valve installed in the oven. The column oven was held isocratic at 80 °C for 8 min, and the helium carrier gas had a 65 mL/min flow rate (1.448 bar). Calibrations were made with certified ISGAS standards (%v/v) of at least three levels for nitrogen (5 % up to 20 %), methane and ethane (15 % up to 100 %) having a certified accuracy of 5 %. The uncertainty associated with the certified gas standards and calibration curve was not accounted for in the reported composition uncertainties. The errors considered in the reported composition uncertainties is the standard deviation from conducting multiple composition measurements from one or more gas sampling bags for each data point and the error associated with the vapor headspace on the liquid trap extraction plumbing. The composition accuracy reported in Table 6.1 was found using the largest reported uncertainty.
The solenoid valve used in the liquid trap would occasionally experience leakage, which could ultimately bias the composition of the measurements. Measurements with detectable leakage have been noted. To reduce the effects of valve leakage, an effort was made to equalize the pressure on each side of the valve to reduce the flow potential.

6.4 Effervescence Measurements

Measurements were conducted for Titan sea temperatures ranging from 92 K to 96 K and varying methane-ethane-nitrogen compositions to cover the range of sea conditions that exist on Titan. Pressures were varied from 1.5 bar to 4.5 bar to account for varying sea depths. The twelve effervescence measurements and their respective uncertainties are presented in Table 6.2. All reported uncertainties have a coverage factor of 2. A detailed discussion of the uncertainties can be found in Chapter 7.
Table 6.2: Effervescence measurements of methane-ethane-nitrogen mixtures.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>87.1 ±0.3</td>
<td>0.0</td>
<td>12.9 ±0.3</td>
<td>1.546 ±0.007</td>
<td>96.2 ±0.5</td>
<td>101.4 ±0.8</td>
<td>10830 ±1435</td>
</tr>
<tr>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>87.7 ±0.2</td>
<td>0.0</td>
<td>12.3 ±0.2</td>
<td>1.65 ±0.01</td>
<td>93.5 ±0.5</td>
<td>100.2 ±0.8</td>
<td>13029 ±1639</td>
</tr>
<tr>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>82.5 ±0.5</td>
<td>0.0</td>
<td>17.5 ±0.5</td>
<td>1.782 ±0.007</td>
<td>95.9 ±0.5</td>
<td>99.6 ±0.8</td>
<td>3257 ±819</td>
</tr>
<tr>
<td>4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>72.3 ±0.5</td>
<td>0.0</td>
<td>27.7 ±0.5</td>
<td>4.53 ±0.08</td>
<td>97.0 ±0.5</td>
<td>104.1 ±0.8</td>
<td>17915 ±1806</td>
</tr>
<tr>
<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0</td>
<td>97.3 ±0.1</td>
<td>2.7 ±0.1</td>
<td>1.73 ±0.05</td>
<td>103.6 ±0.6</td>
<td>118.7 ±0.8</td>
<td>28810 ±2381</td>
</tr>
<tr>
<td>6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0</td>
<td>94.6 ±0.6</td>
<td>5.4 ±0.6</td>
<td>4.41 ±0.05</td>
<td>92.5 ±0.5</td>
<td>107.2 ±0.9</td>
<td>24559 ±2136</td>
</tr>
<tr>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50.6 ±0.3</td>
<td>44.2 ±0.2</td>
<td>5.2 ±0.2</td>
<td>1.85 ±0.01</td>
<td>97.8 ±0.5</td>
<td>108.7 ±0.8</td>
<td>18729 ±1887</td>
</tr>
<tr>
<td>8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>57.5 ±0.2</td>
<td>37.2 ±0.1</td>
<td>5.3 ±0.2</td>
<td>1.561 ±0.007</td>
<td>92.7 ±0.5</td>
<td>107.8 ±0.8</td>
<td>26448 ±2298</td>
</tr>
<tr>
<td>9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>47.6 ±0.4</td>
<td>30.9 ±0.4</td>
<td>21.5 ±0.3</td>
<td>3.21 ±0.02</td>
<td>91.9 ±0.5</td>
<td>97.8 ±0.8</td>
<td>11074 ±1396</td>
</tr>
<tr>
<td>10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>24.9 ±0.1</td>
<td>48.3 ±0.4</td>
<td>26.8 ±0.4</td>
<td>3.44 ±0.03</td>
<td>91.9 ±0.5</td>
<td>94.2 ±0.8</td>
<td>2475 ±656</td>
</tr>
<tr>
<td>11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>27.0 ±0.5</td>
<td>61.4 ±0.5</td>
<td>11.6 ±0.5</td>
<td>3.85 ±0.03</td>
<td>91.8 ±0.5</td>
<td>98.8 ±0.8</td>
<td>10244 ±1394</td>
</tr>
<tr>
<td>12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30.2 ±0.3</td>
<td>63.9 ±0.3</td>
<td>5.9 ±0.3</td>
<td>2.133 ±0.007</td>
<td>93.6 ±0.5</td>
<td>111.6 ±0.8</td>
<td>31758 ±2465</td>
</tr>
</tbody>
</table>

<sup>a</sup> Leakage through the solenoid valve may have biased the composition more than the reported uncertainty.<br><sup>b</sup> Unable to achieve effervescence.
Measurements 1-5 and 7 allowed the temperature of the liquid mixture and heater surface to stabilize before increasing the heater power as discussed above in Section 6.2. As a result, several of the sea temperatures were higher than anticipated because the cryocooler was unable to remove the amount of heat that was being added to the liquid by the cartridge heater while maintaining the desired temperature. Measurements 6 and 8-12 rapidly increased the heater power until effervescence occurred.

Measurements 3 and 10 show a significantly lower heat flux and temperature differential between the heater surface and sea. Effervescence for measurement 3 was recorded for a very small stream of bubbles coming from a single point on the heater. Measurement 10 was conducted under poor visibility and was determined when there was significant disturbance to the liquid-vapor interface. It is possible this was due to another phenomenon other than effervescence such as a release of bubbles from the liquid trap which would mean that this point was conducted prematurely. The authors recommend reviewing the videos of effervescence for each of the data points to visualize the variability in effervescence for each measurement. The effervescence videos can be viewed at http://hdl.handle.net/2376/12183.

Measurements 1, 3, and 12 experienced detectable leakage through the solenoid valve. This could have potentially biased the composition measurement as liquid from the test cell could flow into the liquid trap and vice versa. As a result the uncertainty associated with the composition of these measurements may be higher than the reported values.

Effervescence was not achieved for measurement 5. The upper voltage limit of the power supply was reached before effervescence occurred. However severe convection currents were visible near the cartridge heater which may have a negative impact on submarine operations and instrument readings. Nonetheless, bubble incipience data in Table 6.2 are consistent with
solubility limits for liquid ethane and liquid methane; due to the lower solubility of nitrogen in ethane, there are fewer bubbles available to come out of solution requiring more heat for bubble incipience. The inverse is true for higher liquid methane seas.

From the Phase 1 Titan Submarine (Hartwig et al., 2016), the waste heat flux into the Titan seas was estimated to be 370 W/m² from a detailed thermal balance between radioisotope generator power source, internal insulation, and coolant distribution network. Examination of Table 6.2 shows that the lowest recorded heat flux at the point of bubble incipience is nearly an order of magnitude higher. This implies that the current submarine design has nearly an order of 10 safety factor on the resultant waste heat needed to produce bubbles which would interfere with science instruments or propellers.

6.5 Freezing Point Depression Measurements

Upon completion of the effervescence measurements, two freezing point depression measurements were conducted. Though ice buoyancy and formation relevant to Titan has previously been investigated, these measurements were necessary to verify predictive models in the literature and to provide experimental data for current Titan sea property models (e.g. Thompson, 1985; Roe and Grundy, 2012; Prokhvatilov and Yantsevich, 1983; Hofgartner and Lunine, 2013). The same experimental setup was used for the freezing measurements. The experimental procedure was also kept the same except instead of adding heat to achieve effervescence; the test cell and liquid were allowed to continue to cool until ice began to form. The results of the freezing point measurements are presented in Table 6.3.
Table 6.3: Freezing point depression measurements.

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Methane [mol %]</th>
<th>Ethane [mol %]</th>
<th>Nitrogen [mol %]</th>
<th>Pressure [bar]</th>
<th>Sea Temp. [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>61.0 ±0.1</td>
<td>25.6 ±0.1</td>
<td>13.4 ±0.1</td>
<td>0.290 ±0.007</td>
<td>71.5 ±0.5</td>
</tr>
<tr>
<td>F2</td>
<td>46.9 ±0.2</td>
<td>45.3 ±0.1</td>
<td>7.9 ±0.3</td>
<td>0.517 ±0.007</td>
<td>74.0 ±0.5</td>
</tr>
</tbody>
</table>

The freezing point depression measurements show dramatic subcooling below the triple point temperatures of methane (90.7 K) and ethane (90.4 K) (Lemmon et al., 2013). The first freezing point measurement F1 could not be confirmed visually due to severe fogging on the borescope lens. Instead freezing was determined using the temperature and pressure measurements. The onset of freezing was determined when the pressure stopped decreasing similar to what was observed by Guildner et al. (1976). At the onset of freezing the temperature of the liquid stopped decreasing and stayed constant and then slightly increased. The slight temperature increasing is likely due to the liquid mixture being subcooled before a nucleus could form for solidification.

Freezing point F2 was verified visually using the video camera and borescope. The video is available at http://hdl.handle.net/2376/12183 and shows the growth of a solid white ice ball within the test cell at a temperature of 74 K and pressure of 0.517 bar. The pressure and temperature showed similar behavior to freezing point F1.

The freezing liquid line was depressed more than 15 K below the triple point temperatures of pure ethane. Though there are only two measurements, this data suggests that freezing will occur at higher temperatures for ethane-rich mixtures.
6.6 Conclusions

The likelihood of effervescence in a methane-ethane-nitrogen mixture increases with nitrogen content. At conditions similar to the surface of Ligeia Mare (93 K, 1.5 bar, and 70 mol % methane), effervescence will not occur unless the surface of the submarine approaches 105 K. Effervescence in ethane-nitrogen mixtures was only achieved for temperature differences between the submarine surface and sea greater than 14 K.

It was discovered that nitrogen will slowly come out of solution without causing effervescence if heating is done slowly over several minutes. When the heater power was ramped slowly, the pressure in the sealed test cell would continue to rise as the temperature of the liquid increased due to nitrogen coming out of the liquid. Furthermore the temperature rake measured a significant thermal gradient between liquid below the heater and liquid above the heater. This suggests that heat and bubbles radiating out from the submarine will rise up and away from the submarine making them less likely to interfere with instrumentation and maneuverability. These effects occur at lower heat fluxes and smaller temperature differences between the sea and submarine surface for methane-rich mixtures. Thus, for the most conservative design of the thermal systems, assume sea property of pure methane with dissolved nitrogen. Nevertheless, results show that there is an appreciable safety factor on the resultant heat into the liquid before the point of bubble incipience for current waste heat fluxes.

Acknowledgements

The authors would like to thank Jonathan Lomber of Washington State University for developing the gas composition analysis procedure and providing a brief description of the
process. The authors also thank Alex Dunsmoor for conducting the composition measurements. The authors thank Emily Richardson for conducting the video editing. This work was supported by NASA Space Technology Research Fellowship grant NNX14AL59H and NASA research grant NNC16MF93P.
References


The uncertainty analysis conducted throughout this research followed the standards and guidance outlined by Coleman and Steel (2009) and the National Institute of Standards and Technology (Taylor and Kayutt, 1994). The combined standard uncertainty \( u_c \) was determined using

\[
uc = \left( u_{\text{systematic}}^2 + u_{\text{random}}^2 \right)^{1/2}
\]

(7.1)

where \( u_{\text{systematic}} \) is the systematic source of errors, also known as the bias error, and \( u_{\text{random}} \) accounts for the random sources of errors. Uncertainty propagation was conducted utilizing

\[
u_Y = \sqrt{\sum_i \left( \frac{\partial Y}{\partial X_i} \right)^2 u_{X_i}^2}
\]

(7.2)

where the variable \( Y \) is a function of \( X \), and \( u \) represents the uncertainty of the variable. The reported expanded uncertainties \( U \) were determined using a coverage factor of 2 \( (k = 2) \) where \( U = ku_c \) and thus have a 95 % level of confidence. The individual uncertainties and sources of errors for each of the experimental measurements are discussed below.

7.1 Pressure Measurements

Two different Paroscientific Digiquartz Pressure Transducers were used over the course of this work. The model 1000-500A transducer has an absolute range of 0-500 psia with a typical accuracy of 0.05 psi. The model 410K-101 has an absolute range of 0-10,000 psia with a typical accuracy of 1 psi. Both transducers had been fully calibrated within the last 2 years.
Repeatability errors were found by conducting seven pressure readings over the course of a PρT-x measurement and typically three measurements during an effervescence measurement.

7.2 Temperature Measurements

Three different temperature sensors were used over the course this work. A LakeShore germanium resistance temperature sensor GR-1400-CD was used for measuring temperatures in the PρT-x measurements. The typical sensor accuracy is ±4 mK at 4.2 K and ±15 mK at 77 K. A linear accuracy curve was regressed from the manufacturer’s specifications to provide the estimated accuracy at the measured temperature. A Cryo-con silicon diode was used to measure the surface temperature of the cartridge heater in the effervescence measurements. The uncalibrated silicon diode uncertainty in the temperature range from 77 K to 300 K is ±0.25 K. LakeShore platinum resistance temperature diodes (RTDs) PT-100 were used to measure the liquid temperatures in the effervescence measurements. The PT-100 sensors were calibrated using SoftCal and have a typical accuracy of ±0.25 K in the temperature range from 70 K to 305 K. Repeatability errors were determined by conducting seven temperature readings over the course of a PρT-x measurement and typically three readings during a effervescence measurement.

7.3 Composition Measurements

The helium-hydrogen composition measurements were collected by pressure feeding the liquid out of the bottom of the test cell, flowing it through a plumbing manifold where it would
vaporize, and collecting the vapor in a 1 L gas sampling bag. This method assumes that the composition is constant as the liquid mixture flows out of the test cell and vaporizes. The first 5 to 10 seconds of flow was vented before the vapor was collected in the sampling bag. This was done to ensure the vapor mixture in the extraction tube was flushed from the lines and to allow enough time to flush the barbed connection on the gas sampling bag to ensure air does not get into the bag. The gas sampling bags were filled then evacuated three times with 99.999 % pure hydrogen prior to filling with a sample. The helium-hydrogen samples were analyzed using a Varian CP-3800 GC system with a thermal conductivity detector to quantify the concentrations of helium and hydrogen gases. The gas chromatograph utilizes a Silcosteel HaysSepQ 80/100 mesh packed column (18ft X 0.125in; Supelco). The method used for this analysis incorporated a 10μL stainless steel injection loop controlled by a Valco switching valve installed in the oven. The column oven was held isocratic at 45 °C for 6 min, and the nitrogen carrier gas had a 65 mL/min flow rate (21 psi). Calibrations were made with certified standards (%v/v) of at least four levels for helium (25% up to 75%) and hydrogen (25% up to 100%). The certified standards were prepared by Airgas with a certified accuracy of 0.02 mole %. The reproducibility was determined by analyzing each gas sample three times and calculating the standard deviation.

Methane-ethane-nitrogen composition measurements were analyzed using the same gas chromatograph but the technique used to extract the liquid sample was updated to utilize the liquid trap that was described in Chapters 6. The gas sampling bags were flushed a minimum of three times before being filled with a sample to be analyzed using a gas chromatograph at Washington State University’s Analytical Chemistry Service Center. A Varian CP-3800 GC system with a thermal conductivity detector was used to quantify nitrogen and a flame ionization detector was used to quantify the methane and ethane gases. The column and injection loop that
was used for helium-hydrogen measurements was also used for methane-ethane-nitrogen measurements. The column oven was held isocratic at 80 °C for 8 min, and the helium carrier gas had a 65 mL/min flow rate (21 psi). Calibrations were made with certified standards (%v/v) of at least three levels for nitrogen (5 % up to 20 %), methane and ethane (15 % up to 100 %). The certified standards were prepared by ISGAS with a certified accuracy of 5 mole %. The accuracy of the calibration curve and certified calibration gases was not included in the reported uncertainties of the methane-ethane-nitrogen composition measurements.

For the methane-ethane-nitrogen composition measurements, vapor samples were collected in two or three different sample bags and each sample bag was analyzed a minimum of two times to determine the reproducibility error. There were no statistical discrepancies between different bags of the same sample.

As discussed in Chapter 6, the liquid trap had the potential to bias the composition measurements. The SV91, normally open, Valcor solenoid valve would occasionally experience leakage due to an imperfect seal between the plunger and the seal disc. Once the PρT-x or effervescence measurement data had been recorded and the liquid needed to be collected for a composition measurement, the solenoid valve would be actuated. This separates the liquid within the test cell and the liquid within the trap and begins pumping 9 W of heat into the trap. The temperature and thus the pressure of the trap increased significantly faster than the test cell due to the relatively small thermal mass. As the liquid vaporized, the liquid in the trap was collected in a sampling cylinder to avoid over-pressurizing the liquid trap. The vapor on the test cell side of the solenoid valve was vented to maintain approximately equal pressures on each side of the solenoid valve. Since the liquid mixtures in the test cell and liquid trap vaporized at different rates, a composition difference could occur, especially near the saturation temperatures of
methane and ethane. Thus any leakage through the valve could influence the composition of the measurement. Leakage effects were minimized by keeping the pressure on each side of the solenoid valve approximately equal to minimize flow potential. Unfortunately, leakage through the valve could not be detected until after the sample was collected and captured within the sampling cylinder. Leakage was detected by venting the pressure on one side of the valve to create a pressure differential of approximately 40 psi. The experimenter would then wait 10 to 30 minutes to note any measurable change in the pressure. Measurements that had leakage through the valve were noted. These measurements were discarded or noted as having a potential composition bias larger than the reported uncertainty. Additional composition bias was also introduced from the liquid trap extraction plumbing. The liquid trap used to collect a composition sample had a liquid volume of 18 ±1 ml not including the internal volume associated with the solenoid valve that was neglected. The stainless steel tube that was used to pressure feed the liquid out of the liquid trap into the sampling cylinder contained a gaseous mixture not representative of the liquid since the tube has a thermal gradient from the testing temperature of the liquid trap to room temperature. For helium-hydrogen mixtures this portion of the tubing was flushed out of the system before the gas sample was captured. However with the introduction of the liquid trap, this volume of vapor was captured in the sampling cylinder which introduces bias into the composition measurement. For the methane-ethane-nitrogen PpT-x measurements the gaseous volume including the high pressure stainless steel extraction tube and subsequent needle valve was approximately 1 ml. The connection to the valve, which was nearly all of the 1 ml volume, was at room temperature. The potential bias in the composition was dependent on the moles in this volume which was determined based on the pressure of the fluid and assuming the 1 ml vapor volume within the valve connection was at room temperature. The
maximum uncertainty for the methane-ethane-nitrogen PpT-x measurements due to the vapor headspace was 0.1 mol %. The effervescence measurements had a different extraction manifold that had a volume of 6 ml. This introduced a maximum uncertainty of 0.3 mol % to the composition measurement at the highest pressure.

The reported compositions have been normalized so the sum of the components equals 100 percent as the sums of the raw compositions from the gas chromatograph were slightly above or below 100 percent. This is done by dividing the raw composition by the raw total composition and multiplying by 100 percent.

7.4 Effervescence Heat Flux at Incipience

The heater power was measured using a HP 6438B DC power supply. A constant voltage was supplied through a resistance cartridge heater that simulated the Titan Submarine. The resulting current was a function of the voltage and resistance. The power supply has a load effect of 60 mV and the dial gauges have a readability of ±0.25 V and ±0.025 A. These errors were propagated through the power equation

\[ P = V \times I \quad (7.3) \]

where \( P \) is the power in watts, \( V \) is the voltage in volts, and \( I \) is the current in amps. The propagated power uncertainty is then determined by

\[ u_P = \sqrt{(V)^2 u_I^2 + (I)^2 u_V^2} \quad (7.4) \]

where \( u_P \) is the uncertainty of the power, \( u_I \) is the uncertainty of the current measurement, and \( u_V \) is the uncertainty of the voltage measurement.
The cylindrical cartridge heater has a diameter of 7.62 mm and length of 50.04 mm. Both dimensions were measured five times using calipers with an accuracy of 0.01 mm and averaged. The ends of the heater were not considered in the surface area because one end was used for the electrical leads, insulation, and sealant while the other end of the heater was covered in epoxy and had a silicon diode thermally anchored to it which would significantly reduce the heat flux compared to the stainless steel heater body. The flat end of the heater has a surface area of 4.8E-5 m² while the long curved body has a surface area of 1.2E-3 m². Thus it was assumed that the heat flux at the ends of the cylinder could be neglected. The error from the power and the surface area of the heater were propagated through the heat flux equation

\[ \phi = \frac{P}{A_{\text{surface}}} \]  

(7.5)

where \( \phi \) is the heat flux in W/m² and \( A_{\text{surface}} \) is the surface area in m². The surface area is given by

\[ A_{\text{surface}} = \pi D * L \]  

(7.6)

where \( D \) is the diameter and \( L \) is the length. Note the ends of the cylinder have been neglected.

The uncertainty in the surface area, \( u_{A_{\text{surface}}} \), was found using

\[ u_{A_{\text{surface}}} = \sqrt{\left(\pi D\right)^2 u_L^2 + \left(\pi L\right)^2 u_D^2} \]  

(7.7)

where \( u_L \) is the uncertainty in the length measurement and \( u_D \) is the uncertainty in the diameter measurement. The uncertainty in the heat flux, \( u_\phi \), was then found using

\[ u_\phi = \sqrt{\left(\frac{1}{A_{\text{surface}}}\right)^2 u_P^2 + \left(-P * A_{\text{surface}}^{-2}\right)^2 u_{A_{\text{surface}}}^2} \]  

(7.8)
7.5 Density Measurements

A single-sinker densimeter with magnetic suspension coupling was used to determine the fluid density as shown by McLinden et al. (2007) and discussed in Chapter 2. The uncertainty of a magnetic suspension balance, such as the one used in this work, has been extensively studied by McLinden and Splett (2008). This system uses a Mettler Toledo AT261 balance which has a 0.010 mg precision. This precision was never realized given the operating environment of the balance. The balance experiences significant vibrations from the coldhead of the cryocooler and vacuum pumps.

The single-sinker densimeter method has several inherent uncertainty contributions, some of which can be calibrated and accounted for. The Force Transmission Error (FTE) \( \phi_0 \) associated with the magnetic coupling can be accounted for by conducting measurements in vacuum over the applicable temperature range before and after the fluid run. The FTE minus one \( \phi_0 - 1 \) is generally less than \( \pm 2.0 \times 10^{-5} \) throughout this work. This is consistent with values reported by McLinden et al. (2007). The balance error is also accounted for during each measurement using tare weights of equal volume and different masses. The balance error was found to be \( \alpha = 0.99968 \).

The uncertainty associated with the mass and volume calibration of the fused quartz sinker discussed in Chapters 2 and 3 has also been accounted for. The thermal contraction of fused quartz was also accounted for using the equation developed by Okaji et al. (1995) which has a standard deviation of \( 1.6 \times 10^{-8} \text{ K}^{-1} \). The uncertainty in the sinker was propagated through the density calculation and factored into the overall uncertainty in the calculated fluid density.

Ten balance readings were conducted for each measurement position throughout the density measurement. The repeatability of the balance reading was the largest uncertainty in the
density measurements. For the PρT-x methane-ethane-nitrogen measurements conducted above 90 K, the Measure Point 1 position of this specific magnetic suspension system became unstable under certain fluid conditions and would experience oscillations as large as 5 milligrams. This stems from the Rubotherm controller that supplies power to the electromagnet. The power would vary sinusoidally causing the permanent magnet and thus the force transmitted to the balance to oscillate around the steady state balance reading. This caused a large uncertainty in some of the density measurements for the methane-ethane-nitrogen mixtures.

7.6 Summary of Uncertainties

The PρT-x experimental system used in this research is believed to be the only system in the world currently capably of conducting measurements below 90 K (Richter et al., 2016). To achieve temperatures below liquid nitrogen temperatures, sacrifices were made in the accuracy of the measurements which led to relatively large uncertainties for reference quality measurements. Uncertainties were minimized as much as possible for the available budget and equipment.

PρT-x measurement uncertainties may be reported as a single value in terms of the density. This is done by combining the uncertainty associated with the temperature, pressure, density, and composition measurement. The method for combining PρT-x measurements is outlined by Richter and McLinden (2014).
References


CHAPTER 8 - CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Two primary questions were investigated throughout this work: 1. Does dissolved helium pressurant in liquid hydrogen propellant have a significant effect on the propellant tank performance? 2. How will dissolved gaseous nitrogen in the methane-ethane seas of Titan affect the design of the Titan Submarine? Both relate to the fundamental problem of characterizing dissolved gases in cryogenic liquid fuels. The conclusions of this research and recommendations for future work are presented in the sections below.

8.1 Dissolved Helium in Liquid Hydrogen Propellant

Parahydrogen-helium Pressure-Density-Temperature-Composition measurements were conducted from 17 to 29 K for pressures up to 305 psia (2.1 MPa). These measurements were used to develop the first mixture equation of state for hydrogen-helium. This EOS was implemented into GFSSP to determine the effects of dissolved helium in liquid hydrogen on a propellant tank performance. Dissolved helium pressurant did not affect the pressurization rate of a liquid hydrogen propellant tank. However, the rate at which the liquid propellant temperature increased was reduced. While developing the self-pressurization model in Chapter 4, it was discovered that the uncertainty associated with the heat transfer coefficients for cryogenic hydrogen had a larger effect on the pressurization model than dissolved helium. The natural convection heat transfer coefficient correlations used in this work were classical models which contain general constants. Liquid hydrogen and saturated hydrogen vapor behave much differently than traditional fluids. Additional work should be done to develop accurate heat transfer coefficient models for liquid hydrogen and cryogenic gaseous hydrogen. Updated
correlations would improve the accuracy of liquid hydrogen propellant tank modeling. It should be noted that the fundamental findings of this work remain valid even with the uncertainty in the heat transfer coefficients.

Current helium-hydrogen solubility models are only valid for steady state problems and cannot account for the rate helium dissolves into or degasses from liquid hydrogen. This work provides evidence to suggest that the rate at which helium degasses from liquid hydrogen is very slow due to the transport properties of the mixture. It may take hours or days for the tank to achieve a steady pressure as helium slowly degasses. This was observed by NASA engineers and scientists while monitoring the pressurization rate of the Evolvable Cryogenics (eCryo) Engineering Design Unit (EDU) tank (Stephens, 2016). They found that a tank filled with liquid hydrogen behaves differently than a tank that contains liquid nitrogen or oxygen when it is pressurized with gaseous helium. Figures 8.1 and 8.2 show the pressurization of the EDU tank with helium pressurant when it is filled with liquid hydrogen (Figure 8.1) and liquid nitrogen (Figure 8.2). Figures 8.1 and 8.2 were developed for NASA’s eCryo program by J. R. Stephens (2016) and show the pressurization of the EDU tank with helium. The red curve shows the tank pressure versus time when ambient temperature helium pressurant is injected into the ullage. The green curve shows the tank pressure versus time when ambient temperature helium pressurant is injected through a diffuser submerged in the liquid. The initial tank pressure was approximately atmospheric pressure (14.7 psia). A valve was opened allowing helium pressurant to flow into the tank, causing the pressure to increase. If the pressure exceeded the predetermined cut off pressure (32.0 psia for hydrogen and 38.5 psia for nitrogen), the valve was closed, stopping the flow of helium. The tank pressure then decreased as the helium pressurant cools and exchanges heat with the tank and liquid. If the pressure dropped below a predetermined pressure (31.0 psi
for hydrogen and 37.5 psia for nitrogen), the valve was re-opened, allowing helium pressurant to flow into the tank, increasing the EDU tank pressure, as seen by the stepped increase in pressure. This process was repeated until the rate at which the EDU tank pressure decreased was sufficiently small to conduct a subsequent experiment.

Figure 8.1: Liquid Hydrogen Filled Tank – comparison of the pressurization of the tank ullage with gaseous helium when the pressurant is injected directly into the ullage (red) versus injected through a submerged diffuser (green).
A major revelation occurred when helium was injected through a submerged diffuser in liquid hydrogen, denoted by the green line in Figure 8.1, which although beyond the scope of this work, may warrant further investigation to determine whether the phenomenon has implications for propellant tank performance. Approximately 550 % more helium (1.52 lbm vs. 0.28 lbm) was required to achieve the 32 psia tank pressure when helium was injected through the submerged diffuser versus being injected into the ullage. This phenomenon was not seen with liquid nitrogen (Figure 8.2), or liquid oxygen, which was also tested but not plotted. For liquid nitrogen and liquid oxygen, approximately equal amounts of helium pressurant were required to achieve the desired pressure whether the helium was injected into the ullage or through the submerged diffuser.
In the past, this phenomenon has been incorrectly attributed to thermodynamic effects. The logic being that helium injected through the submerged diffuser is considerably colder by the time it reaches the ullage compared to being injected directly into the ullage. The colder pressurant has a greater density, thus requiring more pressurant in order to achieve a specified pressure. There are two inherent flaws with this logic:

1. The pressurant will achieve thermal equilibrium with the tank walls and liquid, and thus the location of the pressurant injection is irrelevant if transport properties do not have an effect on the system.

2. For a purely thermodynamic effect, the behavior of the pressurization curve would be the same regardless of the cryogenic fluid. The effect would not be as pronounced with fluids such as liquid nitrogen or liquid oxygen since they are not as cold as liquid hydrogen and thus do not have as large of an effect on the pressurant density. Regardless which cryogenic fluid is used, the helium pressurant should behave similarly if this is purely a thermal effect.

The eCryo program showed experimentally that tank pressurization behaves very differently when gaseous helium was injected through the submerged diffuser into liquid hydrogen (green line in Figure 8.1) versus liquid nitrogen (green line in Figure 8.2). The pressurization of the liquid nitrogen filled tank in Figure 8.2 behaves consistently with thermodynamic expectations. When helium is injected into the ullage (red line) or submerged diffuser (green line), the tank pressure increases rapidly until the pressure limit was exceeded and the valve closed. The EDU tank pressure then decreased as the pressurant achieved thermal equilibrium with the tank walls and liquid.
The pressurization of the liquid hydrogen filled tank in Figure 8.1 showed similar behavior to the liquid nitrogen filled scenario when helium pressurant was injected into the ullage (red line) but not when it was injected through the submerged diffuser (green line). The pressurization curve for the submerged diffuser in liquid hydrogen (green line in Figure 8.1) increased rapidly when the valve was opened. Once the tank reaches 32 psia the valve was closed and the pressure dropped as the helium cooled and reached thermal equilibrium within the tank and liquid. The pressure then begins to slowly increase. The pressurization rate is much faster than can be attributed to heat leak into the tank alone. The self-pressurization model described in Chapter 4 showed that a comparable tank only saw a 0.7 psia pressure increase over the course of 10 hours. The continued pressurization of the tank after the valve was closed in Figure 8.1 is due to helium pressurant degassing out of the liquid hydrogen following injection through the submerged diffuser. The dissolved helium will slowly come out of solution until tank achieves equilibrium. This transport phenomenon should not be unexpected as the solubility model developed by Zimmerli et al. (2010) showed that helium does not dissolve in liquid nitrogen or liquid oxygen but will dissolve in liquid hydrogen.

As a result of the above revelation, an attempt was made to qualitatively reproduce the results of NASA’s EDU pressurization tests, utilizing the same experimental apparatus used to conduct the parahydrogen-helium PpT-x measurements described in Chapters 2 and 3, with limited success. To reproduce the EDU experiment, liquid hydrogen was condensed in the test cell and room temperature helium gas was bubbled through the bottom of the test cell. The test cell was then sealed and the pressure of the test cell was observed. This was also done for liquid nitrogen. The results for liquid hydrogen (left) and liquid nitrogen (right) are shown in Figure 8.3.
Figure 8.3: Pressurization curves of gaseous helium bubbled up through liquid hydrogen (left) and liquid nitrogen (right).

Figure 8.3 shows distinct pressure spikes for liquid hydrogen (left) that occurred during the course of thermal equilibration. These pressure spikes are believed to be the result of helium being suddenly released to ullage. It is possible that the phenomenon shown in Figure 8.3 is a small-scale version of what NASA scientists were observing in the EDU tank. This phenomenon was not observed in liquid nitrogen. Though this phenomenon is likely dependent on the experimental apparatus that was used, it highlights the unique interactions that exist between liquid hydrogen and helium pressurant.

Solubility models show that small amounts of helium will dissolve in liquid hydrogen (Zimmerli et al., 2010). Though the amount is small (0.17 mole % at 30 psia and -423°F), the effects of the dissolved pressurant can be unexpected and significant. The solubility model of Zimmerli et al. (2010) and the EOS developed in Chapter 3 are only valid for equilibrium conditions and do not account for the transport properties of helium in liquid hydrogen.
8.2 Recommendations for Future Work Concerning Dissolved Helium in Liquid Hydrogen

This work does not provide a conclusive answer to whether dissolved helium in liquid hydrogen has a significant effect on propellant tank properties. Not enough experimental data is available. It can be concluded that for a traditional mission utilizing liquid hydrogen with a propellant tank pressure of approximately 30 psia and duration of several hours or less, dissolved helium in liquid hydrogen propellant does not have a significant effect on the tank performance. This cannot be said with confidence for higher propellant tank pressures or longer mission durations as larger quantities of helium may dissolve into the liquid propellant which could cause issues in subsequent components such as cavitation in the turbopumps. The time dependence of dissolved helium in liquid hydrogen and the significant differences that occur when pressurant is injected into the ullage versus a submerged diffuser is also discussed. It is clear that injecting helium into the ullage results in more predictable tank behavior. As discussed in Section 8.1, injecting helium pressurant into the liquid propellant can lead to a larger helium concentration than equilibrium solubility models can predict (Zimmerli et al., 2010), and is a logically undesirable condition.

If helium continues to be used as a pressurant for liquid hydrogen rocket propellant for longer duration missions such as fueling depots and traveling to the moon, the effects of dissolved helium in liquid hydrogen need to be investigated further and better understood. Experiments should be conducted to determine under what conditions and helium mole fraction cavitation will occur and the transport properties of helium-hydrogen mixtures should be studied.
8.3 Methane-Ethane-Nitrogen Measurement to Support the Titan Submarine

Pressure- Density-Temperature-Composition, effervescence, and freezing point depression measurements of methane-ethane-nitrogen mixtures were conducted for conditions applicable to the seas on Saturn’s moon Titan. These measurements provided the foundation for modelling efforts to design the Titan Submarine, which NASA will use to explore the depths of Kraken Mare and Ligeia Mare.

The results highlighted in Chapters 5 and 6 show that nitrogen solubility increases with increased pressure and decreased temperature. The liquid density increases with increased pressure, decreased temperature, and increased ethane concentration. The effervescence measurements concluded that the waste heat for the current Titan Submarine design has a safety factor of 10 before nitrogen bubbles would begin to interfere with science instruments. The measurements also showed that heat and nitrogen bubbles from any hot zones on the submarine will dissipate upward. This further reduces the risk of negative impact on the instruments and maneuverability.

The most intriguing revelation was the degree of freezing point depression that was seen in methane-ethane-nitrogen mixtures. Though only two measurements were conducted, the freezing liquid line was depressed more than 15 K below the triple point temperatures of pure ethane. Historically, significant research and discussion has occurred regarding the conditions under which ice will form on Titan and whether ice will sink or float. The freezing point depression results should influence NASA scientists’ and engineers’ considerations regarding ice on Titan and how it may affect the Titan Submarine as it explores the seas. More measurements
should be conducted to fill out the freezing liquid line of methane-ethane-nitrogen mixtures to fully understand the conditions under which ice will form on Titan.

This experimental system was not originally designed for freezing point measurements. As a result the system could not maintain the desired pressure as the fluid mixture continued to cool. Redesigning the plumbing manifold to include a pressure regulator from the nitrogen pressurant tank could solve this problem. Additionally the borescope lens froze over during the first freezing point measurement, which could be prevented in the future by adding a heater on the end of the borescope. To improve the methane-ethane-nitrogen composition measurements, additional calibration gas mixtures should be purchased to increase the confidence and accuracy of the gas chromatograph calibration curve. Furthermore, the technique used to obtain the liquid composition measurements was subject to bias if the solenoid valve did not completely seal. Conducting the composition measurement in situ would be ideal but would require a capillary extraction tube paired with a gas chromatograph system. If this experimental system is to be used going forward it would be cost effective to invest in a more robust composition extraction and measurement method.

8.4 Recommendations for Future Methane-Ethane-Nitrogen Measurements to Support the Titan Submarine

It was concluded that nitrogen effervescence in liquid methane-ethane mixtures will not be a major concern for the thermal design of the Titan Submarine. Furthermore it was confirmed that there is significant depression of the freezing point in methane-ethane-nitrogen mixtures which will influence scientific discussions regarding the potential for ice formation in the seas of Titan. Additional freezing point depression measurements should be conducted to fill out the
solidus line. The composition measurements should be conducted in situ with the extraction method and gas chromatograph incorporated into the experimental system to increase the accuracy of the measurements. The measurements conducted in this work have provided the foundation for continued advancement of Titan Submarine design work related to the ballast systems, onboard scientific instrumentation, and propulsion system.
References
