HYDROGEN STORAGE CAPACITY OF TETRAHYDROFURAN AND
TETRA-N-BUTYLAMMONIUM BROMIDE HYDRATES
AT FAVORABLE THERMODYNAMIC CONDITIONS

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Acknowledgments

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From the bottom of my heart I’d like to thank my family, I love you all. Without your prayers and continued support I wouldn’t be here today. Words cannot express how grateful I am for the love you have given me and continue to give me throughout this journey of life.
Abstract

An exploratory investigation was conducted to evaluate the feasibility of employing binary hydrates as a medium for H$_2$ storage. Two reagents, tetrahydrofuran, (THF) and tetra-n-butylammonium bromide (TBAB), which had been reported previously to have potential to form binary hydrates with H$_2$ at favorable conditions (i.e., low pressures and high temperatures), were investigated.

A scale-up facility was employed to quantify the hydrogen storage capacity of THF binary hydrate. Gas chromatograph (GC) and pressure drop analyses indicated that the weight percentages of H$_2$ in hydrate were less than 0.1%. This is well below the current USDOE target of 5.5 wt. % for transportation applications.

To summarize, the major conclusions of this investigation are:

- H$_2$ can be stored in binary hydrates at relatively modest pressures and temperatures which are probably feasible for transportation applications.
- The storage capacity of H$_2$ in binary hydrate formed from aqueous solutions of THF over a concentration range extending from 2.78 to 8.34 mol % and at temperatures above 263 K and pressures below 11 MPa was < 0.1 wt. %.
- Under-saturated solutions of THF appeared to have the highest H$_2$ storage capacity.
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Chapter 1: Introduction

1.1 Chapter Overview

Chapter 1 provides general information regarding gas hydrates, beginning with an overview in section 1.2. Section 1.2.1 discusses the importance of hydrogen hydrates followed by a brief literature review of previous experimental and theoretical studies done on hydrogen storage in binary hydrates (section 1.2.2). Technical objectives for this thesis are presented in section 1.3 followed by the overview of the thesis in section 1.4.

1.2 Background

The discovery of gas hydrates can be accredited to chemist Joseph Priestly, who first encountered sulfur dioxide (SO$_2$) hydrate in 1778. Priestly, known for discovering gases such as oxygen, hydrogen, carbon and sulfur dioxide, was studying the freezing of water in the presence of different gases (Priestly, 1778). While bubbling sulfur dioxide into water at low temperatures he observed gas and water molecules transformed into an ice-like solid structure, which would later become known as a gas hydrate.

A gas hydrate is a special type of clathrate in which water molecules form solid cages that enclose trapped guest molecules, as shown in Figure 1.1 (von Stackelberg and Muller, 1954). Under appropriate thermodynamic conditions (typically, elevated pressure and/or low temperature), water molecules assemble into stable hydrogen bonded crystal lattices having different configurations depending on the size of the guest molecule. Guest molecules diffuse into the water cages and are stabilized within them by Van der Waals forces (Du et al., 2011). All common gas hydrates form one of three
cubic crystal structures shown in Figure 1.1: structure I (sI), structure II (sII) or structure H (sH).

Each hydrate (unit-cell) structure is composed of a combination of small (pentagonal dodecahedron), medium (tetrakaidecahedron) and large (hexakaidecahedron) cages. Many different gas molecules are capable of forming hydrates including, but not limited to, CO$_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, H$_2$, N$_2$, O$_2$, N$_2$, Ar, and H$_2$S.

The unit cell of sI hydrate consists of 2 pentagonal dodecahedrons ($5^{12}$) and 6 hexakaidecahedron ($5^{12}6^2$) cages composed of 46 water molecules. sI typically forms with guest molecules having characteristic diameters, $d$, between 4.2Å and 6Å, such as methane, ethane and carbon dioxide (Sloan, 2008). Smaller molecules ($d < 4.2$Å) such as nitrogen and hydrogen form sII hydrates as do larger molecules ($6$Å $< d < 7$Å) such as propane and iso-pentane. A combination hydrate, structure H, forms with even larger molecules such as iso-pentane or neohexane ($7$Å $< d < 8$Å).

Figure 1.1 Common hydrate structures. Source: Journal of Geological Research, vol. 2011.
Hydrates remained largely a chemical curiosity until the mid-1930’s, when Hammershmidt (1934) identified gas hydrates as being the cause of blockages in natural gas pipelines. Hydrate research activities increased temporarily until appropriate solutions (i.e., de-watering of the gas and the use of methanol inhibitors) were identified. Pipelines transporting natural gas offshore (at depths greater than 600 m) or in cold climates are at ideal conditions to form agglomerates of solid hydrates which can cause the pipe to clog or rupture. Figure 1.2 shows a photograph of a pipeline hydrate plug. These plugs cost oil companies millions of dollars each year due to operational shutdowns and, in some instances, have resulted in loss of life.

Figure 1.2 A natural gas hydrate core formed in an oil pipeline. Source: Petrobras (Brazil).
In the 1960’s, a Russian drilling crew in the Messoyakha gas field struck methane hydrate. It was the first of a series of discoveries that revealed potentially huge natural reservoirs of methane hydrate in permafrost areas and beneath the ocean floor at depths over 500 m. The amount of natural gas that exists as hydrate is a subject of continuing debate (Milkov, 2004), but considering that estimates of its abundance are between $10^{12}$ and $10^{17}$ standard cubic feet ($2.8 \times 10^{10}$-$2.8 \times 10^{13}$ m$^3$), it has been suggested that hydrates represent a significant untapped energy resource (Demibras, 2010). As a result, research on gas hydrates, primarily methane and carbon dioxide, has intensified and National programs have been established in Japan, India, and the U.S. Recently, in March 2012, Japanese researchers successfully produced natural gas from an offshore methane hydrate well drilled at an ocean depth of 1000 m in the Nanakai Trough (Figure 1.4).

![Map showing global gas hydrates](image)

**Figure 1.3** Location of global gas hydrates. Source: USGS.gov
1.2.1 Hydrogen Hydrate

Historically, it was believed that hydrogen molecules were too small and mobile to form hydrates, but in 1999 Dyadin et al. (1999) confirmed the existence of H₂ hydrate at pressures of 300-400 MPa and temperatures around 293 K. Further experiments performed by Mao et al. (2007) reveal that H₂ gas generates s-II hydrates at 200 MPa and 250K, with two H₂ molecules occupying small cages and four H₂ molecules occupying larger cages.
1.2.2 Previous Work

There is interest in employing pure H₂ hydrate as an energy storage medium for transportation applications; however, the very high pressures required to form and maintain these hydrates pose a problem. A major breakthrough to significantly reduce the equilibrium pressure of hydrogen hydrate has been to add a reagent such as tetra-n-butylammonium bromide (TBAB; \( C_{16}H_{36}NBr \)) to water. Hashimoto (2008) demonstrated that adding small amounts of TBAB reduced hydrogen hydrate formation pressure from 350 MPa to ~1MPa at 280K. TBAB is a salt that forms a semi-clathrate hydrate crystal (\( C_{16}H_{36}N^+\timesBr\times38H₂O \)) under atmospheric pressure and near room temperature with a unit-cell composed of 16 S-cages (small) and 8 L-cages (large). The bromide anion constructs cage structures with water molecules while the cation occupies empty L-cages (Shimada et al., 2005). At moderate pressures and temperatures (e.g., 1 MPa and 280K), hydrogen molecules can be stabilized and trapped within available empty S-cages (Lee et al., 2005).

Tetrahydrofuran (THF; \( C₄H₈O \)) has also been reported to reduce hydrogen hydrate formation pressures (Lee et al., 2005). THF is a water miscible organic liquid compound that generates structure II hydrates at 278K at 0.1 MPa (Hawkins & Davidson, 1966). According to Lee et al. (2005), THF hydrate can store about 4 wt.% H₂ at 12 MPa and 270K; however, recent experiments by Ogata et al. (2008) suggest that, at similar conditions, stoichiometric THF hydrate can store only 0.26 wt.% H₂.
1.3 Motivation

Hydrogen is the most abundant element in the universe and can be produced domestically from natural gas, reducing our dependence on imported fossil fuels. Employing hydrogen hydrate as an energy carrier has attracted interest due to several advantages (Florusse, 2004). For example, unlike methane hydrate, pure hydrogen hydrate burns clean, producing no greenhouse gas carbon emissions, making this a favorable clean alternative fuel.

The primary advantage of H₂ storage in hydrates is that, unlike metal hydrides, which must undergo a chemical reaction (often having slow kinetics and requiring heating up to 473K) to release hydrogen fuel, hydrates undergo a rapid phase transformation (i.e., melting), making them ideal for onboard use in fuel cell vehicles and other specialized applications.

The greatest uncertainty related to onboard hydrogen hydrate storage for transportation applications is energy density. Currently, the U.S. Department of Energy has set a 2015 target of 5.5 wt. % hydrogen storage in hydrates (Mao et al., 2007). Theoretical studies performed to date by Willow and Xantheas (2012) suggest that hydrates may be able to store up to 5.3 wt. % hydrogen; however, no experimental data exist to validate these results.

Since binary hydrates, such as those employing TBAB and THF, can store H₂ at considerably lower pressure than pure H₂ hydrate, their use in transportation applications appears to warrant investigation. Previous studies of the hydrogen storage capacity of binaryH₂ hydrates have produced conflicting results. The present study was undertaken to accurately quantify this important parameter.
1.4 Technical Objectives

The overall goal of my thesis research was to explore the feasibility of employing binary hydrates as a medium for H₂ storage. Candidate protocols to form binary hydrogen hydrates with the potential for high H₂ storage capacity (at relatively low formation pressure and high formations temperatures) were identified via a series of exploratory experiments that employed a Differential Scanning Calorimeter (DSC) and Raman spectroscopy system. H₂ wt.% could not be accurately determined in the small-scale DSC tests, so these formation protocols were scaled up to produce samples large enough to measure the hydrogen content (gm H₂/gm hydrate) of the selected binary hydrates.

The primary hypothesis that was tested is: binary hydrates can store H₂ gas at acceptable energy densities at moderate pressures and temperatures for transportation applications.
Chapter 2: Facilities

2.1 Chapter Overview

Chapter 2 discusses the experimental facilities used to investigate binary hydrogen hydrate formation. A description of the differential scanning calorimeter is presented in Section 2.2 followed by the Raman spectroscopy system in Section 2.3. The hydrate synthesis scale up facility is discussed in Section 2.4.

2.2 Calorimeter System

For these experiments a TA Instruments Multi-Cell Differential Scanning Calorimeter (MCDSC) was used to identify candidate protocols to form binary hydrogen hydrates at moderate temperatures and pressures. A photograph of the MCDSC facility is shown in Figure 2.1 followed by a schematic diagram of the system in Figure 2.2.

Differential scanning calorimetry is a technique used to determine the thermal properties of materials such as heat capacity or the energy of chemical reactions, phase changes and phase transitions. During an experiment, small ampoules containing a sample and a reference that does not contain the substance being tested are heated or cooled at a controlled rate while the difference in thermal power required to maintain them at the same temperature is monitored. These data can be plotted as functions of temperature or time.
Figure 2.1 MCDSC setup.
Figure 2.2 Schematic drawing of the calorimeter setup.
Figure 2.3 shows a cross-sectional view of the differential scanning calorimeter (DSC) that includes the major components. Built into the DSC are four thermo-electric-device (TED) detectors (G) which are mounted to a shared heat sink (A) and controlled by a resistance temperature detector (RTD) sensor (B) or scanned by the Scan TED (C). A 1 kΩ platinum RTD (F) monitors the DSC temperature. Precise temperature control over the range of 233K-423K is achieved using a combination of an electric heater and a cascade of Peltier coolers (D) along with a circulating water bath which serves as a hot side reference for the cooler. The 17.2 mm o.d. x 16.6 mm tall cylindrical sample cells (ampoules) have an internal volume of 0.5 mL and are made of Hastelloy, which provide excellent resistance to corrosion. Maximum operating pressure is 41.5 MPa (6000 psig). Figure 2.4 is a photograph of a sample cell showing the top closure that is fitted with a tube that allows the addition or removal of different gases.

Figure 2.3 Internal view of the MCDSC thermal components.
The TA Instruments MCDSC is equipped with three sample cells and one reference cell, allowing the user to perform multiple tests simultaneously. The MCDSC can detect heat flows down to about 0.2 \( \mu \text{W} \). Table 2.1 summarizes the instrument’s performance specifications provided by the manufacturer.

<table>
<thead>
<tr>
<th>Sample Cells</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Cells</td>
<td>1</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>-40 to 150 (^{\circ})C</td>
</tr>
<tr>
<td>Detection Limit</td>
<td>0.2 ( \mu \text{W} )</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>1 ml</td>
</tr>
<tr>
<td>Sample Volume</td>
<td>up to 1 ml (See Note)</td>
</tr>
<tr>
<td>Short Term Noise Level</td>
<td>0.2 ( \mu \text{W} )</td>
</tr>
<tr>
<td>Baseline Repeatability</td>
<td>2 ( \mu \text{W} )</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>0 (isothermal) to 2 (^{\circ})C/minute</td>
</tr>
<tr>
<td>Response Time</td>
<td>90 second time constant or 9 minutes for 99% response</td>
</tr>
<tr>
<td>Heat Measurement Method</td>
<td>Heat flux</td>
</tr>
</tbody>
</table>

Table 2.1 Manufactures specifications for the MCDSC. Note: The sample volume for pressure cells are 0.5 mL.
Figure 2.5 shows the components used to pressurize the MCDSC samples. Research Grade 4.8 (99.998% purity) N\textsubscript{2} and ultra-high purity grade 5.0 (99.999% purity) H\textsubscript{2} were employed in the experiments. N\textsubscript{2} was used to purge the system of oxidizing gas before addition of the combustible H\textsubscript{2}. Dry N\textsubscript{2} gas also is constantly circulated within the calorimeter to prevent condensation from occurring when operating at temperatures below the dew point of the ambient air. H\textsubscript{2} was used to form the gas hydrates. Since the commercial gas cylinder pressure was 13.79 MPa, a manual pressure generator from High Pressure Equipment Company was utilized to increase the pressure of the sample above this value. The pressure generator has a stroke capacity of 60 cm\textsuperscript{3} per stroke and a maximum working pressure of 34 MPa. A 100 cm\textsuperscript{3} buffer tank (i.e., high pressure stainless steel gas reservoir) was used to minimize pressure swings in the sample cell during the experiment due to the consumption of gas during hydrate formation or small leakage from valves and connections. System pressure is monitored with both a bourdon tube pressure gauge and an electronic pressure transducer (Omega Engineering model PX309). The pressure transducer had an operating range of 0 to 13.79 MPa and an accuracy of 2% full-scale.
2.3 Raman spectroscopy system

Raman spectroscopy was employed to verify hydrogen hydrate formation. A photograph of the system is provided in Figure 2.6. Primary components include a solid-state laser, notch filter, spectrograph, and charged couple device (CCD) detector. Fused silica optical fibers are used to transmit laser radiation into, and Raman shifted radiation out of a high pressure sample cell with an internal volume of 12 ml. Figure 2.7 shows the fiberoptic probe connected to the sample cell. A schematic diagram of the Raman system is provided in Figure 2.8.
Figure 2.6 Raman spectroscopy setup.

Figure 2.7 High pressure sample cell with gas line and fiber optic attachments.
Raman spectroscopy is an analytical technique used to observe vibrational, rotational and other low-frequency modes of energy in a system based on light scattering detection. In this technique, molecules are excited to a virtual energy state by laser photons. A portion of the excited molecules relax down to different rotation or vibrational levels than where they originally existed, with the emission of a photon. The frequency of the photon is shifted from the laser radiation. This Raman shift is
determined by the structure of the molecule; i.e., its particular rotational and vibrational levels.

For these experiments, the sample is irradiated by a single-frequency diode-pumped solid-state laser (ALPHALAS GmbH Model MONOLAS-532-100-SM) with maximum continuous (cw) power output of 100 mW at a wavelength of 532 nm. The laser light is transmitted into the sample cell with an optical fiber probe. Energy is transferred to the molecules through inelastic collisions. Raman shifted radiation is collected by the probe composed of seven 200 μm core UV silica fibers encased in epoxy within a 3.18 mm (0.125 in.) o.d. stainless steel tube (Figure 2.9). The probe passes through a compression fitting installed in the sample cell closure to prevent gas leakage. The center fiber, labeled (a), is used to bring in light from the laser, while the six surrounding fibers, denoted as (b), collect scattered light and transmit it to the spectrometer. The probe diameter was too small to include focusing optical components at the ends of the fibers, so the laser radiation exiting the transmitting fiber diverges in a cone of light determined by the difference in the refractive indices of the fiber core and cladding (i.e., the acceptance cone). Similarly, the field of view of the collection fibers is defined by the overlap of the acceptance cones of the ring of six fibers.

Figure 2.9 Cross-sectional view of the fiber optic probe. Light from the laser is transmitted into the sample cell by fiber (a), the surrounding six fibers (b) collect scattered light.
Prior to entering the spectrograph, collected light from the sample cell passes through a collimating lens, notch filter and focusing lens as shown in Figure 2.10. Since most of the light collected by the probe is reflected laser radiation, the notch filter removes radiation at 532±0.6 nm and allows Raman shifted light to pass into the spectrograph.

![Notch filter assembly](image)

**Figure 2.10** Notch filter assembly.

A focusing lens directs the Raman shifted light onto a narrow slit at the entrance to the spectrograph. The present experiments employed a Princeton Instruments SpectraPro-2750 with a focal length of 0.750 m. A collimating mirror within the spectrograph directs light entering the instrument through the adjustable inlet slit onto a diffraction grating. For these experiments, gratings of 300, 1200 and 1800 nm were available. The grating has a series of equally-spaced grooves bladed into its surface which disperse photons, according to their wavenumbers, onto on focusing mirror directed toward a charged couple device (CCD) detector. This detector is composed of an array of light-sensitive capacitors that digitalize light intensities. The Princeton Instruments PIXIS 2K (Model number 7533-0001) camera detector employs a 2048 x
512 pixel imaging array. By employing an array of pixels, a relatively wide spectral range can be captured simultaneously, unlike a single element photomultiplier which samples small intervals of a spectrum sequentially as the diffraction grating is rotated. The output of the camera is stored and displayed on computer.

2.4 Scale-up facility

The calorimeter and Raman facilities examine small samples of hydrate, typically of the order of a few cm³ or less. Quantitative measurements of H₂ content by analysis of gas collected after decomposing the hydrate are difficult to perform accurately with such small quantities. Consequently, a scale-up hydrate synthesis facility, shown in Figure 2.11, was constructed for this purpose. The facility has a maximum working pressure of 17 MPa. The operating temperature range is 243K to 298K. A schematic diagram is presented in Figure 2.12.
Figure 2.11 Scale up facility used to synthesize and collect hydrate gas samples.
Figure 2.12 Layout of the scale up facility.
Hydrate samples are formed in a HiP tubular series reactor (Model TOC-20) inside a laboratory freezer shown in Figure 2.13. The stainless steel tubular reactor has an internal volume of 0.5L and maximum working pressure of 34 MPa. A 51 cm long PTFE stainless pipe with and i.d. of 0.4 cm is inserted into the reactor to isolate the hydrate samples from the reactor walls. Pressure is monitored with Omega Engineering pressure transducers (PT) (model PX309) teed into lines connected to both the upper and lower closures of the reactor. Gas temperature is monitored with a thermistor (Omega Engineering Model TJ36-44004) inserted into the gas line emerging from the lower closure. Pressurized gases used to purge the system or to form the hydrate are precooled inside two 300 cm$^3$ buffer tanks (i.e., stainless steel sample cylinders) located behind the reactor in Figure 2.13. Precooling minimizes changes in temperature of the sample during the experiment. Gas flow into the reactor is controlled using the panel shown on the right hand side of the photograph.
It was necessary to increase the pressure of the purge N\textsubscript{2} gas and H\textsubscript{2} gas used to form the hydrate above levels in the supply tanks (commercial gas cylinders). A bladder accumulator was employed for this purpose. Outside the freezer, bottled N\textsubscript{2} or H\textsubscript{2} gas flows into the shell of a 1 gallon accumulator purchased from Accumulators Inc. Water is pumped manually from a reservoir into an elastomer bladder contained inside the metal accumulator shell. As the bladder expands, it compresses the surrounding gas in the shell, increasing its pressure. Pressurized gas exits from the bottom of the accumulator and fills the buffer tanks inside the freezer.
After hydrate is formed in the sample chamber and before it is decomposed to collect the released gas, the head space in the chamber and the gas lines are purged with N₂ to eliminate as much of the H₂ gas as possible, since residual H₂ complicates the determination of the hydrogen content of the hydrate. Care is exercised to minimize variations in the sample pressure (by means of a back pressure regulator) and temperature (by using precooled gas from the buffer tank) during the purge. After the lines and headspace are cleared of H₂, the system is brought to room temperature to allow the hydrate to fully dissociate. Flow exits the top of the sample chamber and passes through a 3-way valve that directs the gas either to collection chambers or a vent as shown in Figure 2.14. There are two collection ports; one to take 50 cm³ samples and another to collect 3.8L samples. Gas samples collected during the purge and after hydrate decomposition are analyzed with the Shimadzu 14A gas chromatograph (GC) shown in Figure 2.15.

The present tests employed helium as a carrier to transport the sample gas through the GC separation column. A thermal conductivity detector (TCD) was used to identify gas species in the eluted sample.
Figure 2.14 Gas collection setup. Below are two addition 3.8L containers used to collect gas samples.

Figure 2.15 Gas chromatography setup.
Chapter 3: Experimental Procedures

3.1 Chapter Overview

Chapter 3 describes the experimental procedures that were developed to form binary hydrogen hydrates and measure their properties. The protocols that were followed to perform the MCDSC and Raman spectroscopy experiments are reported in Sections 3.2.1 and 3.2.3. Methods employed for scale-up tests to quantify hydrate storage capacity are discussed in Section 3.2.4.

3.2 Hydrate synthesis protocol

Aqueous solutions used to form gas hydrates are prepared by mixing distilled and deionized water with appropriate quantities of reagent grade THF (99.99%) or TBAB (99.99%) to achieve the desired concentrations. In this study, three different concentrations of THF (2.78, 5.56 and 8.34 mol %) and two concentrations of TBAB (1.38 and 3.59 mol %) were investigated at gauge pressures of 0, 6.89, 10.34 and 13.79 MPa.

The apparatus shown in Figure 3.1 was used to generate hydrate particles from the THF or TBAB solutions. The white PVC column is filled with a solution of THF or TBAB and closed. An aerosol spray is generated from a nozzle installed in the bottom of the column by pressurization of the liquid with N₂ gas. Directly beneath the nozzle is a bucket containing liquid N₂. Tiny droplets of the solution contact the cold liquid N₂ and immediately form hydrate particles. The particles are placed inside the laboratory freezer equipped with a glove box (Figure 3.2) and held at 262K while being sieved using the
stack shown in Figure 3.3. Particles \( \leq 210 \, \mu m \) in size are collected and used in the experiments.

Figure 3.1 Apparatus used to generate THF and TBAB hydrate crystals.

Figure 3.2 Freezer used to homogenize size of hydrate particles.
To form H$_2$ binary hydrates, a pressure cell is loaded with either liquid THF or TBAB solution or the fine hydrate crystals produced from these solutions and slowly pressurized with ultra-high purity Grade 5.0 H$_2$ gas provided by Airgas. Well-defined safety procedures are followed when working with the combustible H$_2$ gas. Prior to pressurizing the cells, the system is purged with Grade 4.8 N$_2$ and evacuated with a vacuum pump to remove any oxidizing gases. Combustible gas detectors are installed in the laboratory to monitor for leaks.
3.2.1 MCDSC experiments

The MCDSC requires sample cells to be loaded into the instrument at room temperature. This prevents condensation from occurring in the calorimeter and affecting the thermo-electric detectors, but also precludes the use of fine THF or TBAB crystals which will quickly melt. Hence, for the MCDSC experiments, gas hydrates are formed from liquid solutions of THF or TBAB.

The high pressure MCDSC sample cells shown in Figure 3.4 are filled with a recorded mass of solution (approximately 0.25 g) and placed into the thermal well of the calorimeter. Gas lines are purged with N\textsubscript{2}, then evacuated and finally pressurized with H\textsubscript{2}. Each of the five THF and TBAB solutions were tested at gauge pressures of 0, 6.89, 10.34 and 13.79 MPa.

The temperature time-history shown in Figure 3.5 was applied to cycle the samples between 263K and 293K (-10 °C and 20°C). Binary hydrate nucleation and growth occurs as the solution is cooled from room temperature to 263K at a rate of 2K/min and held for two hours. Ice formation also occurs. Next, the samples are allowed to fully dissociate by increasing the temperature from 263K to 293K at a rate of 0.1K/min. This thermal cycling is repeated two more times to minimize any start-up transients and maximize hydrate yield. The results of the MCDSC experiments are presented and discussed in the following chapter.
Figure 3.4 MCDSC high pressure sample cells.

Figure 3.5 Temperature schedule for MCDSC experiment.
3.2.2 Raman spectroscopy experiments

Best candidate solutions to form H\textsubscript{2} binary hydrates were identified from the MCDSC experiments and verified using Raman spectroscopy. Spectra of the tested samples were taken for the three different phases that exist in the cell: liquid, gas and hydrate.

In these experiments, fine THF or TBAB hydrate crystals are synthesized following the procedure described in Section 3.2. Approximately 10 g of crystals are loaded into the sample cell shown in Figure 3.6. The top closure of the cell is secured and the cell is submerged in a water bath circulating a solution of ethylene glycol at 263K. The sample is then slowly pressurized with H\textsubscript{2} to 10.34 MPa. Inside the cell is a magnetic stirrer that agitates the sample.

Initially, the sample is held at 263K for 24 hours, allowing gas to diffuse into the hydrate cages. Next, the sample temperature is increased to 285K and held for 4 hours. During this time, the gas hydrates start to dissociate and form a liquid-gas interface. A Raman spectrum of the sample is taken at this point in the process.

Gas hydrates are reformed by lowering the sample temperature to 274K and holding for 4 hours. A Raman spectrum is taken to verify hydrate formation. Finally the sample is vented and brought to ambient conditions and one last spectrum is collected of the aqueous solution in the cell. Each of the spectra has a central wavelength of 685 nm using a 1800 nm grating.
3.2.3 Scale-up experiments

THF or TBAB hydrate crystals are sieved down to a size of 210 μm and prepared following the procedure described in Section 3.2. The crystals are packed into a Teflon tube (Figure 3.7) and the mass of the hydrate is recorded. The tube is loaded into the sample chamber located inside the freezer (Figure 2.12) at 263K. Gas flows through the hydrate core via a concentric stainless steel 6.4 mm (1/4”) O.D. tube. The sample is slowly pressurized with precooled H₂ and held at 263K for 12 hrs. Next, the sample is slowly warmed to 277K and held for 4 hours, allowing any ice that formed to melt. Finally, conversion of the remaining liquid to hydrate is allowed to proceed for 24 hours at 274K.
After 24 hours, the hydrate is dissociated and the released gas is collected to determine how much H\textsubscript{2} was stored in the binary hydrate. In order to do this, the H\textsubscript{2} gas surrounding the hydrate in the sample chamber and in the connected gas system must first be removed, since this inventory would overwhelm the H\textsubscript{2} released from the hydrate. A protocol was developed for this purpose and Figure 3.8 shows the various stages of the gas collection process. At State 1, the sample chamber and lines contain pressurized H\textsubscript{2} gas. Between State 1 and State 2, chilled Grade 4.8 N\textsubscript{2} gas is used to purge all or most of the H\textsubscript{2} gas that didn’t get trapped in the hydrate phase from the system. During this purge process, a 1 gallon (3.785 l) gas sampling cylinder is used to collect approximately 7 MPa of mixed hydrogen and nitrogen gas for later analysis. Smaller samples are also
collected at various points in the purge process to confirm that most of the H\textsubscript{2} has been removed. To ensure that there are no significant deviations in system pressure which might lead to hydrate decomposition, the back pressure regulator shown in the Figure is set to the initial sample pressure. At State 3, following the purge, the freezer is turned off and the door is opened to allow the hydrate to fully dissociate at room temperature for 24 hours. As the hydrate dissociates, the trapped H\textsubscript{2} gas is released from hydrate cages, and mixes with the N\textsubscript{2} in the chamber and lines. This gas mixture is collected in sampling cylinders and analyzed using a Shimadzu 14-A GC.

The measured H\textsubscript{2} concentrations in the various gas samples are used to determine the quantity of H\textsubscript{2} stored in hydrate. This is compared with data on the pressure drop that occurs during hydrate formation due to H\textsubscript{2} uptake.

Figure 3.8 Gas purge and sample collection process.
Chapter 4: Results and Discussion

4.1 Chapter Overview

In this chapter, results from MCDSC, Raman spectroscopy, and scale-up experiments are reported and discussed.

4.2 MCDSC Results

The objective of the MCDSC experiments was to identify best candidate protocols to form hydrogen hydrates. Three different concentrations of THF (2.78, 5.56 and 8.34 mol %) and two concentrations of TBAB (1.38 and 3.59 mol %) were compared at pressures of 6.89, 10.37 and 13.79 MPa. In these tests, the calorimeter sample temperature was ramped from 263K to 293K at a constant rate of 0.1K/min. Triplicate experiments were performed for each concentration. In the thermograms that follow, the measured rate of heat flow to or from the sample is plotted as a function of temperature. Heat flows into the sample (endothermic processes) are defined as positive in these Figures.

Results for 2.78 mol % THF are shown in Figures 4.1 through 4.4. An initial test was carried out at atmospheric pressure (without hydrogen) to serve as a baseline. At 2.78 mol % THF, the solution is under-saturated and hydrate formation will result in residual water that will freeze. The thermogram recorded by the calorimeter shown in Figure 4.1 exhibits a large endothermic peak that begins around 273K with a small shoulder that ends at approximately 278K. The apex of the large peak occurs at a temperature of 273.5K and corresponds to ice melting. The small shoulder to the right is
due to decomposition of THF hydrate and its apex occurs at 277K at atmospheric pressure. As seen in the subsequent figures, the binary hydrate (THF + H₂) peak decouples from the ice peak, moving to higher temperatures as pressure increases.

To account for the small differences in the mass of the samples, the measured rates of heat flow shown in the Figures 4.1 through 4.4 were divided by the corresponding sample mass and the constant temperature ramp rate (0.1K/min. = 1.67 x 10⁻³K/s). This yields a heat capacity with units of J/(g•K). Figure 4.5 compares the results for the four cases at 2.78 mol % THF. Unlike the specific (or sensible) heat, the heat capacity data shown in this Figure also include the heats of fusion (i.e., latent heats) of the ice and hydrate phases.

![2.78 mol % THF](image)

**Figure 4.1** Decomposition curve for 2.78 mol % THF at atmospheric pressure.
Figure 4.2 Decomposition curve for 2.78 mol % THF with H₂ at 6.89 MPa.

Figure 4.3 Decomposition curve for 2.78 mol % THF with H₂ at 10.34 MPa.
Figure 4.4 Decomposition curve for 2.78 mol % THF with H\textsubscript{2} at 13.79 MPa.

Figure 4.5 Comparison of decomposition curves for 2.78 mol % THF at various hydrogen pressures.
The curves in Figure 4.5 all exhibit similar, relatively constant values of heat capacity prior to and following completion of melting of the ice and hydrate. Heat capacities following melting are observed to be about twice those measured as the solid ice and hydrate is heated from 263K. This is consistent with the fact that the sensible heats of ice and liquid water (note that the samples are dilute aqueous solutions of THF and comprise mostly water) are approximately 2.1 and 4.2 J/g•K, respectively, over the range of temperatures and pressures investigated in these tests. The curves also display the anticipated shift in the melting point of ice to lower temperatures, and the increase in the melting temperature of hydrate, as pressure increases.

It is desirable to separate the heat capacity data into its constituent sensible heat and latent heat components, in order to try to estimate the portions of the THF solutions that are converted into ice and into hydrate. Unfortunately, this poses several challenges. Although the heating rate is relatively slow (i.e., 1K/10 minutes; 5 hours to complete the ramp from 263K to 298K), kinetic effects are not negligible, as evidenced by the range of temperatures over which ice is observed to melt. Figure 4.6 is a plot of the heat capacity of a sample comprising 0.2541 g of DI water-only at atmospheric pressure. The water was allowed to freeze completely and then the sample temperature was ramped from 263K to 293K at the same constant rate of 0.1K/min. Melting takes place over a 3K to 4K range, which corresponds to a period of 30 to 40 minutes, during which time the sample consists of a mixture of solid ice and liquid water. The sensible heat of this mixture lies between the values for ice (~2.1 J/g K) and water (~4.2 J/g K).
Figure 4.6 Decomposition of ice at atmospheric pressure.

In the case of the THF solutions, the situation is even more complicated. At 263K, the solid phase consists of a mixture of ice and hydrate crystals. These crystals may be well dispersed in one another. As a sample is warmed, the ice portion will begin to melt first, but the adjacent hydrate could act as a thermal insulator or heat sink. If this is the case, then the ice melting process may extend to even higher temperatures than suggested by Figure 4.6 and overlap with the hydrate melting process. Until all the ice and hydrate melts, the sample will consist of an evolving mixture of liquid and solids, complicating the determination of the sensible heat component at any point during the heating process. Moreover, if the ice and hydrate melting events overlap, then the portion of the measured heat capacity minus the sensible heat component will include contributions from the latent heats of the ice and the hydrate.

Several approaches were tested to estimate the latent heats of the ice and hydrate phases. The MCDSC software allows the user to select a baseline for the heat capacity
vs. temperature curves. Figure 4.7 shows an example used to determine the latent heat of fusion of ice. Here, the baseline of the power vs. temperature curve, shown as the fine red line, is assumed to vary linearly from the value immediately preceding melting to the constant value after the ice has been converted completely to liquid water. The heat of fusion of ice calculated using the area under the melting curve and above this baseline is 333 J/g, which compares well with the standard value from the literature of 333.6 J/g.

![constructed baseline](image)

Figure 4.7 Screenshot showing linear baseline used to estimate latent heat of ice.

For cases where both an ice peak and a hydrate peak exist, the MCDSC software provides the user the option to employ a sigmoidal baseline shown as the thin red line in Figure 4.8. This thermogram is for 2.78 mol % THF at 6.89 MPa. Alternatively, the baseline can once again be taken as the straight line connecting the heat flow rate values at the start and end of the melting process, as shown in Figure 4.9. The areas under the ice melting curves and above the two different baselines, multiplied by the temperature...
ramp rate, were 47.5 J using the sigmoidal baseline and 64.5 J using the straight line. This large difference underscores the difficulty in estimating latent heats.

![constructed baseline](image1)

**Figure 4.8** Screenshot showing sigmoidal baseline used to estimate latent heat of ice.

![constructed baseline](image2)

**Figure 4.9** Screenshot showing linear baseline used to estimate latent heat of ice.
Table 4.1 presents information on the THF + H₂ hydrate dissociation for the 2.78 mol % THF solution at the three elevated pressure where this hydrate can form (since no H₂ is added to the sample for the atmospheric pressure case). The Table includes the measured sample mass and the average molecular weight of the solution, calculated by:

\[ \bar{MW}_n = \sum (MW_i \cdot x_i)_n \]  

(4.1)

Where, \( MW_i \) and \( x_i \) are the molecular weight and mole fraction of species \( i \), respectively. \( T_{\text{max}} \) is the temperature corresponding to the apex of the hydrate dissociation peak and \( \Delta H \) is the total thermal energy added to the sample to dissociate the THF + H₂ hydrate component, determined by the method described above (using a sigmoidal baseline for all cases) and expressed per mole of the entire sample. Since the molar heat of fusion, \( \Delta H_f \), of the hydrate phase typically decreases with increasing pressure (cf. Equation 5 and Table 1 in Lirio & Pessoa, 2013), the results in Table 4.1 suggest that a larger fraction of the THF solution forms hydrate at elevated pressure. Note that:

Number of moles hydrate formed/mole THF solution = \( \Delta H / \Delta H_f \).  

(4.2)

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<th>sample mass (g)</th>
<th>Pressures (MPa)</th>
<th>( T_{\text{max}} ) (K)</th>
<th>( \Delta H ) (kJ/mol)</th>
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Table 4.1 Dissociation conditions for 2.78 mol % THF + H₂ hydrate.

Results for 5.56 mol % THF are shown in Figures 4.10 through 4.14. At this concentration, THF and water are at stoichiometric proportions for hydrate formation
which generally has a structure of 1 mole THF:17 moles water (Gough and Davidson, 1971). The baseline atmospheric pressure data are shown in Figure 4.10. Thermograms recorded at elevated hydrogen pressures of 6.89, 10.34 and 13.79 MPa are shown in Figures 4.11, 4.12 and 4.13, respectively. All thermograms exhibit a large endothermic peak near 273K, indicating that ice continues to form even though the solution contains adequate THF to ensure no excess water.

The second peak between 277K-280 K is believed to correspond to the melting of pure THF hydrate. As sample pressure increases, a third peak appears to the right of the THF peak that we posit is due to dissociation of the binary THF + H₂ hydrate component, and not simply a pressure effect. To test this hypothesis, a calorimetry experiment was performed where a 5.56 mol % THF solution was pressurized to 10.34 MPa with pure N₂ gas. The measured thermogram is compared with the thermogram of the 5.56 mol % THF solution pressurized with H₂ in Figure 4.14. At the same elevated pressure, but in the absence of hydrogen, the third peak to the right of the THF peak does not appear. There is, however, another new peak, this time to the left of the THF hydrate peak. Since N₂ also forms hydrates at elevated pressure, this could correspond to the dissociation of a binary THF + N₂ hydrate component.
Figure 4.10 Decomposition curve for 5.56 mol % THF at atmospheric pressure.
Figure 4.11 Decomposition curve for 5.56 mol % THF with H$_2$ at 6.89 MPa.

Figure 4.12 Decomposition curve for 5.56 mol % THF with H$_2$ at 10.34 MPa.
Figure 4.13 Decomposition curve for 5.56 mol % THF with H₂ at 13.79 MPa.

Figure 4.14 Comparison of decomposition curves for 5.56 mol % THF at 10.34 MPa. The blue curve is for pressurization with H₂; the red curve is for pressurization with N₂.
Figure 4.15 compares the calculated heat capacities of the samples. Once again, the expected shifts of the ice peak to lower temperatures and the hydrate peaks to higher temperatures with increasing pressure are evident in the data.

![Graph showing specific heat capacity vs temperature for 5.56 mol % THF + H₂ at various pressures](image)

**Figure 4.15** Comparison of decomposition curves for 5.56 mol % THF at various hydrogen pressures.

The fraction of the solution that forms hydrate at different pressures can be estimated by calculating the area under the ice peak and above a linear baseline to determine the total energy required to melt the ice component. Dividing this by literature values of $\Delta H_f$ of ice yields the mass of the ice component, which is then subtracted from the total mass of the sample. Following this approach, about 35% of the 5.56 mol % THF solution is converted into hydrate at atmospheric pressure. Pressurizing the sample with...
H$_2$ gas increases this percentage to 75%, 76%, and 78% at 6.89, 10.34, and 13.79 MPa, respectively.

Table 4.2 presents information on the THF + H$_2$ hydrate dissociation for the 5.56 mol % THF solution at the three elevated pressures. The Table includes the measured sample mass and the average molecular weight of the solution. $T_{\text{max}}$ is the temperature corresponding to the apex of the second hydrate dissociation peak associated with the H$_2$ hydrate component, and $\Delta H$ is the total thermal energy added to the sample to dissociate this component. $\Delta H$ for the H$_2$ component increases with pressure, suggesting that more hydrogen is bound up in the hydrate.

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Table 4.2 Dissociation conditions for 5.56 mol % THF + H$_2$ hydrate.

Results for 8.34 mol % THF are shown in Figures 4.16 through 4.19. At this concentration, THF is in significant excess of what is needed to form hydrate. The baseline atmospheric pressure data are shown in Figure 4.16. Thermograms recorded at elevated hydrogen pressures of 6.89, 10.34 and 13.79 MPa are shown in Figures 4.17, 4.18 and 4.19, respectively. While there is some evidence of tiny ice peaks near 273K, it is clear that almost all of the solution forms hydrate. Pressurization of the sample with H$_2$ gas again produces a second peak between 280 K-285 K, that becomes more prominent as pressure increases.
Figure 4.16 Decomposition curve for 8.34 mol % THF at atmospheric pressure.

Figure 4.17 Decomposition curve for 8.34 mol % THF with H₂ at 6.89 MPa.
Figure 4.18 Decomposition curve for 8.34 mol % THF with H₂ at 10.34 MPa.

Figure 4.19 Decomposition curve for 8.34 mol % THF with H₂ at 13.79 MPa.

Figure 4.20 compares the calculated heat capacities per unit mass of the initial 8.34 mol % THF solution. Since all the major peaks correspond to hydrate, they shift to higher temperatures with increasing pressure.
Figure 4.20 Comparison of decomposition curves for 5.56 mol % THF at various hydrogen pressures.

Table 4.3 presents information on the THF + H$_2$ hydrate dissociation for the 8.34 mol % THF solution at the three elevated pressures. The Table includes the measured sample mass and the average molecular weight of the solution. $T_{\text{max}}$ is the temperature corresponding to the apex of the two dissociation peaks and $\Delta H$ is the thermal energy added to the sample to melt the associated hydrate component.

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Table 4.3 Dissociation conditions for 8.34 mol % THF + H$_2$ hydrate.
MCDSC experiments were also conducted using aqueous solutions of tetra-n-butylammonium bromide (TBAB). As discussed in Chapter 1, TBAB has been proposed to reduce the formation pressure of H₂ hydrate (Hashimoto, 2010). TBAB is known to form semi-clathrate hydrate in which the water cage is broken to accommodate the large TBAB molecule (Sloan & Koh, 2008). The ratio of TBAB:water in the hydrate has been reported to range from 1:2 to 1:36. 20% and 40% by mass solutions of TBAB were investigated which correspond to 1.38 mol % (~1:72) and 3.59 mol % (~1:27), respectively.

Results for 1.38 mol % TBAB are shown in Figures 4.21 through 4.24. The thermograms exhibit two endothermic peaks, similar to the 2.78 mol % THF case. It can be surmised that the strong peak to the left corresponds to the melting of ice, indicating that the solution is undersaturated with TBAB such that significant excess water exists after the hydrate component forms as the sample is cooled. When the sample is pressurized with H₂ gas the hydrate peak begins to broaden and shift further to the right in the Figures, to higher temperatures. At 13.79 MPa, there is some evidence of a second hydrate decomposition peak.
Figure 4.21 Decomposition cure for 1.38 mol % TBAB at atmospheric pressure.

Figure 4.22 Decomposition cure for 1.38 mol % TBAB with H$_2$ at 6.89 MPa.
Figure 4.23 Decomposition curve for 5.56 mol % THF with H₂ at 10.34 MPa.

Figure 4.24 Decomposition curve for 1.38 mol % TBAB with H₂ at 13.79 MPa.
Figure 4.25 compares the calculated heat capacities per unit mass of the 1.38 mol % TBAB solution. The area of the ice peaks does not appear to change significantly, suggesting that the partitioning of the solution between hydrate and ice is not affected much by increasing pressure.

![Graph showing specific heat capacity vs temperature for 1.38 mol % TBAB at various pressures](image)

Figure 4.25 Comparison of decomposition curves for 1.38 mol % TBAB at various hydrogen pressures.

Table 4.4 presents information on the TBAB + H₂ hydrate dissociation for the 1.38 mol % TBAB solution at the three elevated pressure conditions. The table includes the measured sample mass and the average molecular weight of the solution. Here, $T_{\text{max}}$ is the temperature corresponding to the apex of the hydrate dissociation peak and $\Delta H$ is the total thermal energy added to the sample to dissociate the hydrate.
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Table 4.4 Dissociation conditions for 1.38 mol % TBAB + H$_2$ hydrate.

Results for 3.59 mol % TBAB are shown in Figures 4.26-4.29. No ice peak is detected in these thermograms, indicating that at 3.59 mol % TBAB (i.e., TBAB:water ratio of 1:27), there is no excess water. At this concentration, TBAB has been reported to form two types of hydrates: Type A and Type B (Shimada et al., 2005). The thermograms, however, exhibit three peaks, suggesting three hydrate structures. Since these three peaks can be detected in the atmospheric pressure case where there is no H$_2$ gas, it is unclear to what extent hydrogen is being incorporated into the hydrate matrix.
Figure 4.26 Decomposition cure for 3.59 mol % TBAB at atmospheric pressure.

Figure 4.27 Decomposition cure for 3.59 mol % TBAB with H₂ at 6.89 MPa.
Figure 4.28 Decomposition curve for 3.59 mol % TBAB with H₂ at 10.34 MPa.

Figure 4.29 Decomposition curve for 3.59 mol % TBAB with H₂ at 13.79 MPa.
Figure 4.30 compares the calculated heat capacities per unit mass of the 3.59 mol % TBAB solution. The general shape of the curves does not change significantly with increasing pressure, although there appears to be a slight shift in the relative strengths of the second and third peaks, as well as the expected shift to higher melting temperatures.

Table 4.5 presents information on the TBAB + H₂ hydrate dissociation for the 3.59 mol % TBAB solution at the three elevated pressure conditions. The Table includes the measured sample mass and the average molecular weight of the solution. Here, T_{max} is the temperature corresponding to the apex of the third hydrate dissociation peak and ΔH is the thermal energy added per mole of sample to dissociate the hydrates associated with the two overlapped large peaks on the left. Observe that ΔH varies by <5%.
Table 4.5 Dissociation conditions for 3.59 mol % TBAB + H₂ hydrate.

<table>
<thead>
<tr>
<th>MW (g/mol)</th>
<th>sample mass (g)</th>
<th>Pressure (MPa)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (K)</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.93</td>
<td>0.2556</td>
<td>6.89</td>
<td>288.54</td>
<td>4.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.34</td>
<td>288.76</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.79</td>
<td>289.01</td>
<td>4.72</td>
</tr>
</tbody>
</table>

The MCDSC experiments suggest that pressurization of THF solution with H₂ gas during the hydrate formation process results in significant changes in the dissociation thermograms. At the two higher concentrations of THF, a second hydrate peak appears at temperatures between around 280K and 285K, that increases in strength with increasing pressure. This suggests an additional hydrate structure, possibly due to the incorporation of H₂ into the crystal matrix. On the other hand, thermograms of the TBAB solutions did not exhibit conclusive evidence of changes in structure when pressurized with H₂. While this does not preclude the possibility of binary TBAB + H₂ hydrate formation, it appears that THF may be a slightly better candidate for further investigation of H₂ storage potential. One advantage that TBAB has over THF is the slightly higher melting point of the hydrate (about 4K) at the same pressure.

4.3 Raman Spectroscopy Results

The MCDSC results revealed that an additional hydrate decomposition peak appears when the 5.56 mol % and 8.34 mol % THF solutions were pressurized with H₂.
gas. It was posited that this peak is associated with hydrogen in the hydrate phase. The Raman spectroscopy experiments were performed to test this hypothesis by confirming the existence of H$_2$ binary hydrate under conditions where the thermogram peak was detected.

Following the procedures described in Section 3.2.2, Raman spectra were taken at various stages of the gas hydrate dissociation process. Fine ice crystals of 5.56 mol % THF were slowly pressurized with H$_2$ gas to 6.89 MPa at 263K and an initial spectrum was collected before significant uptake of hydrogen by the solid phase occurred. This spectrum is shown in Figure 4.31, which plots light intensity measured by the CCD detector, in arbitrary units (a.u.), as a function of the Raman shift (cm$^{-1}$).

In the gas phase overlying the ice and (pure) THF hydrate, four peaks are detected at 4128, 4146, 4158, and 4165 cm$^{-1}$ which corresponds to the H-H stretching modes of the H$_2$ molecules. Hydrogen hydrate was then allowed to form according to the protocol described in Section 3.2.2. Figure 4.32 shows a spectrum of the resulting hydrate at 274K. The broad peak around 4133 cm$^{-1}$ was observed previously by Lee et al. (2005) and is due to the entrapment of H$_2$ in small cages of the binary hydrate. The sample was depressurized and vented and a final spectrum was taken of the 5.56 mol % THF solution at 298K for comparison. This spectrum is shown in Figure 4.33. These results appear to confirm the formation of the binary hydrogen hydrate.
Figure 4.31 Raman spectrum of H$_2$ in the gas phase at 263K.

Figure 4.32 Raman spectrum of 5.56 mol % THF at 274K and 6.89 MPa.
Figure 4.33 Raman spectrum of 5.56 mol % THF solution at 298K.

4.4 Scale-up Results

Scale-up experiments were conducted following the procedures described in Section 3.2.3 to estimate the amount of H₂ stored in binary hydrates. Quantifying H₂ content is not possible with the MCDSC. Based on the calorimetry and Raman results, it was determined that THF hydrate had potential to store hydrogen.

Table 4.6 summarizes the H₂ storage capacity of 2.78, 5.56 and 8.34 mol % THF hydrate determined from GC analysis of collected gas samples. In these experiments, the samples were pressurized with pre-cooled H₂ gas to 12 MPa, which falls between the two highest pressures tested with the MCDSC. As described in Section 3.2.3, gas samples collected at the end of the N₂ purge process at 274 K are analyzed to determine the number of moles of any residual H₂ in the gas phase, based on the measured concentration, pressure, temperature, and known volume of gas in the lines and reactor.
head space. This is subtracted from the number of moles of H₂ collected after the hydrate fully dissociates (determined from the GC data) to estimate the amount of hydrogen that was stored in the hydrate.

<table>
<thead>
<tr>
<th>THF concentration (mol %)</th>
<th>Sample size (g)</th>
<th>∆n (mol)</th>
<th>H₂ (g)</th>
<th>Storage capacity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.78</td>
<td>165</td>
<td>0.041</td>
<td>0.083</td>
<td>0.050</td>
</tr>
<tr>
<td>5.56</td>
<td>166</td>
<td>0.022</td>
<td>0.045</td>
<td>0.027</td>
</tr>
<tr>
<td>8.34</td>
<td>168</td>
<td>0.022</td>
<td>0.045</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Table 4.6 Binary hydrogen storage capacity determined from GC analyses.

In Table 4.6, ∆n is the number of moles of hydrogen that is stored in the hydrate sample. The weight % given in the last column on the right is calculated by dividing the total mass of H₂ determined to have been stored in the hydrate by the mass of THF and water loaded into the reactor at the start of the experiment. Based on the MCDSC results, a portion of 2.78 mol % and 5.56 mol % samples probably consisted of ice, rather than hydrate. Since this fraction is unknown, however, the total sample mass was used as a basis for comparison of the results.

These results suggest that, while H₂ can be stored in THF binary hydrate, the yield is low. The weight percentages fall far below the USDOE target of 5.5 weight %. It is interesting to note that the most dilute THF solution (2.78 mol %) had the highest hydrogen storage capacity. The binary gas hydrate formed from this solution released approximately 0.083 g of H₂, corresponding to a 0.05 wt. % storage capacity. Increasing the THF concentration to 5.56 mol % THF lowers the gas storage capacity by a factor of two. For 5.56 mol % THF, dissociation of the hydrate released approximately 0.045 g of H₂, corresponding to 0.027 wt. % storage capacity. The 8.34 mol % THF supersaturated
solution also had a storage capacity of 0.027 wt. %, suggesting that increasing the THF concentration beyond stoichiometric proportions does not improve H$_2$ yield.

In consideration of the unexpectedly low H$_2$ storage capacities determined by gas sampling and analysis, the experimental pressure records were examined to try to estimate H$_2$ gas uptake during the hydrate formation process to confirm these results. During the formation process, a pressure drop occurs at constant temperature due to the entrapment of H$_2$ in S-cages generated by (sII) THF hydrate. Since the volume occupied by the isothermal gas in the reactor is fixed, the change in the number of moles of H$_2$ in the gas results in a decrease in pressure. The Ideal Gas Law was employed to calculate the decrease in moles of H$_2$ from the measured temperature, pressure drop, and known gas volume, using an appropriate compressibility factor:

$$\Delta n = \frac{\Delta P \times V}{Z \times R \times T}$$  \hspace{1cm} (4.2)

Here, $\Delta n$ is the change in the number of moles of H$_2$ due to uptake by the hydrate, $\Delta P$ is the measured pressure drop, $V$ is the volume of the gas space (98.3 cm$^3$) that was determined by filling the closed system with fluid and collecting and measuring the volume of that fluid, $T$ is the measured temperature, $R$ is the gas constant, and $Z$ is the compressibility factor, which is approximately 1.09 at the tested hydrate formation conditions.

The formation process for 2.78 mol % THF is shown in Figure 4.34. At point A, the hydrate is at 11.15 MPa and 274K. As the sample temperature decreases from about 274K to 263K (point B), pressure drops slightly due to the cooling effect. From point B to point C, H$_2$ is drawn into and trapped in the S-cages of the THF hydrate, resulting in a reduction of gas pressure from slightly more than 11 MPa to slightly less than 10.4 MPa.
Applying equation 4.2, this corresponds to the uptake of about 0.060 g of H\textsubscript{2}. The system temperature is then raised to 277K. By comparison with Figure 4.3, this should melt any ice but preserve most of the hydrate. The sample is held at this temperature for 4 hours to promote the formation of more hydrate, then cooled to 274K and held for an additional 24 hours. Figure 4.35 shows a second, smaller pressure drop that is recorded at 274K. During this process, an additional 0.036 g of H\textsubscript{2} is consumed, for a total of 0.096 g. This value compares reasonably well with GC results of 0.083 g of H\textsubscript{2} released during dissociation.

![Figure 4.34 Pressure drop at 263K due to hydrate formation; 2.78 mol % THF.](image)

2.78 mol % THF + H\textsubscript{2} hydrate pressure drop
The formation process for 5.56 mol % THF solution is shown in Figures 4.36 and 4.37. During the initial uptake shown in Figure 4.36, approximately 0.063 g of H$_2$ is drawn into the hydrate sample at a temperature and pressure of 263K and 9.8 MPa, respectively. The sample temperature is then raised to 277K and held for 4 hours, before being cooled to 274K and held for 12 hours. Figure 4.36 shows the second pressure drop that occurs at 274K, which is calculated to correspond to an uptake of 0.013 g H$_2$ from the gas phase. The total mass of H$_2$ consumed during hydrate formation is 0.076 g.
Figure 4.36 Pressure drop at 263K due to hydrate formation; 5.56 mol % THF.

Figure 4.37 Pressure drop at 274K due to hydrate formation; 5.56 mol % THF.
Finally, Figures 4.38 and 4.39 present the drop in H$_2$ gas pressure during the hydrate formation process for 8.34 mol % THF solution. Although no ice is expected to form from this super-saturated solution, the same temperature process was followed as the other two cases to be consistent. From the observed $\Delta P$s, a total of 0.064 g of H$_2$ are calculated to be consumed during hydrate formation, which is slightly less than the amount estimated from the pressure drop data for the 5.56 mol % THF solution. Table 4.7 compares the GC measurements and pressure drop measurements.

Figure 4.38 Pressure drop at 263K due to hydrate formation; 8.34 mol % THF.
Figure 4.39 Pressure drop at 274K due to hydrate formation; 8.34 mol % THF.

Table 4.7 Comparison of hydrogen storage capacity of THF hydrate around 11 MPa

<table>
<thead>
<tr>
<th>THF concentration (mol %)</th>
<th>Sample size (g)</th>
<th>( \text{H}_2 ) (g)</th>
<th>Storage capacity (wt.%)</th>
<th>( \text{H}_2 ) (g)</th>
<th>Storage capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.78</td>
<td>165</td>
<td>0.083</td>
<td>0.050</td>
<td>0.096</td>
<td>0.058</td>
</tr>
<tr>
<td>5.56</td>
<td>166</td>
<td>0.045</td>
<td>0.027</td>
<td>0.076</td>
<td>0.046</td>
</tr>
<tr>
<td>8.34</td>
<td>168</td>
<td>0.045</td>
<td>0.027</td>
<td>0.064</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The quantities of \( \text{H}_2 \) consumed during hydrate formation that are estimated from the pressure drop data, compare reasonably well with the measured amounts released during dissociation. This appears to confirm that, for the conditions examined in this exploratory study, the storage capacity of binary THF + \( \text{H}_2 \) hydrate is very low.
Chapter 5: Conclusions

An exploratory investigation was conducted to evaluate the feasibility of employing binary hydrates as a medium for H₂ storage. The primary hypothesis that was tested was: *binary hydrates can store H₂ gas at acceptable energy densities at moderate pressures and temperatures for transportation applications.*

Two reagents, THF and TBAB, which had been reported previously to have potential to form binary hydrates with H₂, were investigated. Aqueous solutions of THF and TBAB at concentrations extending from under-saturated to super-saturated with respect to proportions needed to form hydrate were tested at pressures up to 13.8 MPa. Results from a series of calorimetry experiments suggested that THF forms a binary hydrate with H₂, while there was no clear evidence of this for TBAB. The measured THF+H₂ hydrate stability data agreed well with the results of Hashimoto (2006) and Anderson (2007). To confirm that binary THF + H₂ hydrates had formed in the calorimetry experiments, Raman spectra were taken at different points of the hydrate synthesis process using a separate facility. The spectra exhibited the signature characteristic of H₂ entrapment in the small cages of binary hydrate.

Based on the calorimetry and Raman results, it was decided to focus on solutions of THF and to conduct scale-up experiments to determine H₂ storage capacity. Three solutions of THF (2.78, 5.56, and 8.34 mol %) were tested at pressures up to about 11 MPa. GC and pressure drop analyses confirmed that H₂ was stored in the solid phase. The measured hydrogen storage capacities, unfortunately, were very low. Weight percentages of H₂ in hydrate were less than 0.1%. Interestingly, the unsaturated solution
of THF appeared to store the most hydrogen. The reason for this is not clear, although it might be posited that this is related to the lower occupancy of the hydrate cages.

The results of this investigation do not support the original hypothesis. While it was confirmed that H₂ can be stored in binary hydrates at modest temperatures and pressures, the energy densities fell well below the USDOE target of 5.5 wt. %.

To summarize, the major conclusions of this investigation are:

- H₂ can be stored in binary hydrates at relatively modest pressures and temperatures which are probably feasible for transportation applications.
- The storage capacity of H₂ in binary hydrate formed from aqueous solutions of THF over a concentration range extending from 2.78 to 8.34 mol % and at temperatures above 263 K and pressures below 11 MPa was < 0.1 wt. %.
- Under-saturated solutions of THF appeared to have the highest H₂ storage capacity.

Although the present results are not encouraging, it is clear that promoters are successful in significantly shifting the operational pressures and temperature of hydrogen hydrates to values that are feasible for a host of H₂ storage applications. In consideration of this, additional work should be performed to confirm and expand the results of this exploratory study and to investigate alternative binary hydrate storage options for H₂. Specific topics include:

- Add surfactants to the solutions, since recent studies have shown that surfactants can promote the formation kinetics of binary hydrates.
- Conduct extended scale-up experiments that include multiple formation and dissociation cycles and longer hold times to overcome kinetic limitations.
• Investigate other under-saturated concentrations of THF to confirm the sensitivity of storage capacity to this parameter.

• Although the calorimetry experiments did not provide definitive evidence of H₂ binary hydrates with TBAB, this possibility was not excluded. It is worthwhile, therefore, to conduct some scale-up tests with TBAB solutions.
References


